

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

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Applicant: DOSAJ, *et al.*  
Filed: 25/AUG/2006  
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Examiner: Johnson, Kevin M.  
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Customer No.: 00137  
For: Method of Selecting Silicon Having Improved Performance

Commissioner for Patents

P.O. Box 1450

Alexandria, VA 22313-1450

**AFFIDAVIT UNDER 37 C.F.R. §1.132**

Sir:

I, Vishu Dutt Dosaj, being duly sworn, say that:

1. I received a Ph.D. degree in chemical engineering from the University of New Brunswick in Fredericton, Canada, in 1974 and a B.S. degree in metallurgical engineering from Indian Institute of Science in 1967.
2. I have been employed by the Dow Corning Corporation at Midland, Michigan, since 1974, during which time I have been engaged in research and development activities in the field of chemical engineering related to silicon. I am a co-inventor of twelve U.S. patents and have authored/co-authored fifty papers and presentations at international conferences.
3. I am an inventor on the above identified application.

4. I have identified the references attached as Exhibits A-F:
- Tuset, J. Kr.; Ottem, L; Livik, R. Silicon for Chemical Industry Geiranger (1992) (attached as Exhibit A);
  - Rein, Richard; Chipman, John Transaction of the Metallurgical Society of AIME 233 (1965), 415 (attached as Exhibit B);
  - Eriksson, Gunnar; Pelton, Arthur D. Metallurgical Transactions B 24B (1993), 807-814 (attached as Exhibit C);
  - Kammel, Von Roland; Winterhager, Helmut Z. Erzbergbau Metallhuettenw., 18 (1965), 917 (attached as Exhibit D);
  - Kawai, Y.; and Shiraishi, Y. Handbook of Physico-chemical Properties at High Temperatures (1989), Table 4-16, page 131 (citing Kozakevitch, P. Rev. Metall., Paris, 57 (1960), 149 (attached as Exhibit E) (citing Machin, J.S.; Yee, T.B.; and Hanna, D.C. J. Am. Ceram. Soc., 35 (1952), 322) and Kozakevitch, P. Rev. Metall., Paris 57(1960), 149; and
  - Levin, Ernest M.; Robbins, Carl R.; and McMurdie "Phase Diagrams for Ceramists: Volume I American Ceramic Society, 1964, Figure 630 (attached as Exhibit F).

5. The references attached as Exhibits A-F were published and would be readily apparent to one skilled in the art to which the patent application identified above pertains at the time of filing.

6. The calculation of slag compositions from Al and Ca impurities would have been known by one with skill in the art at the time of filing the application identified above. Exhibit A shows the availability of such information before the time of filing. Equations (3) and (4) of Exhibits A shows the distribution equilibria in silicon refining. Figure 5 of Exhibit A enables the calculation of slag composition from Ca and Al impurity levels in silicon metalloid. The ternary diagram in Exhibit A is related to actual slag compositions at specific process conditions for silicon

metalloid by the use in the equilibrium calculations of activity coefficients measured at the specific refining temperature conditions for Al and Ca.

7. The relationship between slag composition and slag viscosity, density, and melting point would have been known to one skilled in the art at the time of the filing of the patent application identified above. Exhibit D shows that the relationship between slag composition and slag density was known. Exhibit E shows the relationship between slag composition and slag viscosity was known, and Exhibit F shows the relationship between slag composition and slag melting point was known.
8. Exhibits B and C teach the activities of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{CaO}$  in slag compositions at various process temperatures. Thus, these activities would have been known to one skilled in the art at the time of filing.
9. One skilled in the art would have known how to, based upon the Ca and Al impurity levels in silicon metalloid at equilibrium during refining, determine the slag composition, and, from the slag composition, know how to predict the viscosity, density, and melting point of the slag.
10. Using the relationships and data available at the time of filing the above identified application, one skilled in the art would not be required to conduct undue experimentation to calculate the equilibrium slag composition from known values of Al and Ca impurities. Furthermore, from the data, information and references available and known, one skilled in the art would be able to predict slag properties from slag compositions without any experimentation in many cases.

I declare that all statements made of my own knowledge are true and that all statements made on information and belief are believed to be true. I also declare that, at the time these statements were made, I knew that willful false statements and the like are punishable by a fine

or imprisonment, or both, under § 1001 of Title 18 of the United States Code, and that willful false statements may jeopardize the validity of the application, or any patent issuing from it.

Vishnu Dosal  
Inventor Name

Date: February 26, 2009

**EXHIBIT A**

## PRINCIPLES OF SILICON REFINING

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A review of our present knowledge and understanding of the fundamental chemistry involved in oxidative refining of liquid silicon is given. Data on slag/metal equilibria and solubilities of oxygen and carbon in liquid silicon are given.

### INTRODUCTION

Due to the nature of the silicon itself, the carbothermic process for making silicon

is in principle defined as a slag-free process. This implies that, apart from elements forming gaseous components and volatile metals or metal oxides that are lost with the offgases, the elements entering with the charge materials and the consumable electrodes are expected to be reduced and tapped as constituents of the product metal. A variety of metallic impurities are therefore present, and those usually recorded in commercial products are listed in Table 1.

**Table 1.** Impurity levels in some typical silicon metal products expressed in per cent by weight.

ELEMENTS %	STANDARD MG-SI	REFINED MG-SI	REQUIRED FOR SOG- QUALITY
Si	97.99	> 98.5	> 99.99
Al	< 0.6	0.1-0.5	< 0.0020
Ca	0.2	0.01-0.05	< 0.0005
Ti	0.05	0.05	< 0.0005
C <sup>x)</sup>	0.03	0.02	< 0.0050
Fe	0.3-0.5	0.3-0.5	< 0.0002
Mn	0.03	0.03	< 0.0002
V, Cr, Ni, Cu	0.01-0.5	0.01-0.03	< 0.0002
Co, Mo, Zr	< 0.005	< 0.005	< 0.0002
P	0.005	0.005	< 0.0001
B	0.005	0.004	< 0.0001

x) Mainly present as SiC-inclusions.

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Institute of Inorganic Chemistry, NTH  
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*Aluminium and calcium being the most abundant impurities in the charge besides the iron do not, however, behave as simply as stated above. Aluminium appears as an impurity in both the quartz (or quartzites) and the reduction materials used, the latter being responsible for bringing nearly all the calcium and 50-75% of the total iron. The oxides of these elements when present in the reduction materials are expected to be fairly easily reduced, whereas the alumina, which is diluted in the silica phase, is less available for reduction and tends to accumulate as a viscous silicate melt in the furnace. As this melt is contacted with metal sufficiently high in calcium an exchange reaction takes place that increases the CaO-content and the fluidity of the oxide phase. Occasionally therefore, some slag is tapped together with the metal.*

*This slag, if not left behind in the runner and subsequently removed, will end up in the refining ladle together with contaminations of aluminium or iron that occasionally may be introduced during the tapping procedure.*

*The purpose of the present paper is, however, not to emphasize on the need for quality control on the selection of raw materials and tapping procedures, but to focus on the refining stage of the whole operation in order to point out its limitations and possibilities.*

#### **OPTIONS IN LIQUID METAL REFINING**

*Apart from sophisticated methods like electrolytic and vacuum refining, both of which are to be of interest in connection with the production of solar-grade silicon, there are only two options of practical interest in bulk liquid-metal refining of silicon metal. They are:*

- methods based on oxidation and

#### *slagging of impurities*

- methods based on chlorination and removal of impurities as volatile chlorides

*Both types of methods are effective for the same types of reactive elements such as the alkali and alkaline-earth metals and aluminium. The chlorination process, being the more effective of the two for these elements, appears to also have a certain purification effect on other elements such as chromium, manganese and copper. The process is, however, of less industrial interest owing to the environmental and material problems associated with the use of chlorine and the emission of corrosive metal chlorides. The silicon industry therefore uses only methods that are based on oxidation and slagging of impurities.*

*The oxygen needed for the refining reactions in oxidative refining can be introduced either*

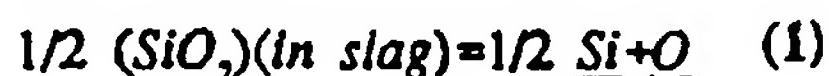
- as a gas in the form of oxygen or air at the metal surface, or by gas-blown through a lance, a nozzle, or plug in the bottom of a refining vessel
- in the form of  $\text{SiO}_2$  as an oxidizing agent

*Gas-blowing is usually combined with addition of some kind of slag-forming compounds that may also act as oxidizing agents. The addition is usually carried out by injection in case a lance is used for gas-blowing, or by direct charging to a top slag in case of the nozzle blowing technique, where intimate mixing associated with air-blowing can be obtained. The various sources of oxygen listed are therefore effective in a real process, but their relative importance may differ from one type of operation to the other. The way the oxygen is introduced does, in fact,*

strongly affect the heat balance and the kinetics of the refining process, but has in principle no influence on the chemical equilibria controlling the process.

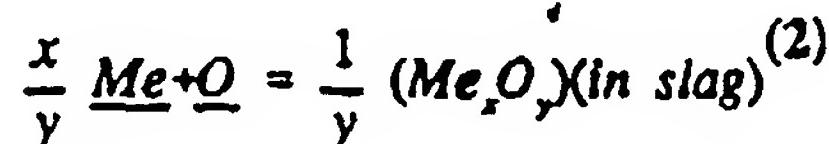
### DISTRIBUTION EQUILIBRIA IN OXIDATIVE REFINING

Now matter how the oxygen is introduced, a boundary-layer oxide film forms at the metal surface as a result of the reaction between oxygen and the most abundant element, which is silicon. The reaction defining the oxygen potential in the metal at this interface is then:

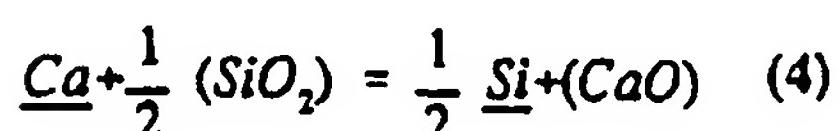
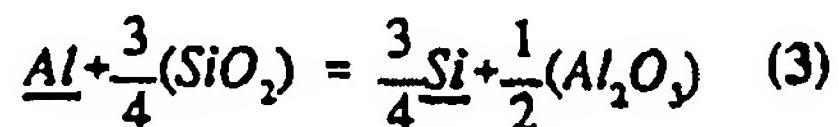


where underlined elements mean elements dissolved in the metal phase.

A dissolved metal impurity Me present at the interface may now react as follows:

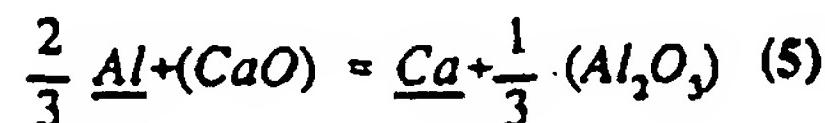


If both reactions are at local equilibrium at the interface, with the same activity of dissolved oxygen ( $a_O$ ), then this quantity can be eliminated if equations (1) and (2) are combined. Multiplication of the resulting expression by the factor  $y/x$  and substituting Me for Al and Ca-yields the following two equations:



This is equivalent to stating that the oxidation of a dissolved impurity is coupled with the oxidation of silicon, since all reactions appear to be under control of the same rate-limiting step, here assumed to be the rate at which oxygen is supplied at the metal-slag

interface. If this is true, it is also evident that the oxidation of the various dissolved elements is mutually coupled through similar reactions: i.e. as follows for the two elements considered:



At low impurity levels, however, the transport of the impurity elements from the bulk of the metal to the slag-metal interface may very well take over as a rate controlling step, and the resulting distribution will deviate from the equilibrium values discussed below.

It has been shown elsewhere that apart from the silicon itself, aluminium and calcium are the only impurities present in metallurgical grade silicon that will contribute significantly to the formation of slag during the oxidation process. Thus, a relevant slag to consider is the ternary system  $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ , and the distribution equilibria expressed by equations (3) and (4) should be related to slags of this type.

Systematic studies of these equilibria have unfortunately not been done for silicon, but have been carried out for ferrosilicon (Fe 75Si) in presence of ternary slags <sup>11</sup>. The results for ferrosilicon based on experimental and calculated data at 1550°C are given as isoconcentration lines for calcium and aluminium in Figure 1 and 2 respectively.

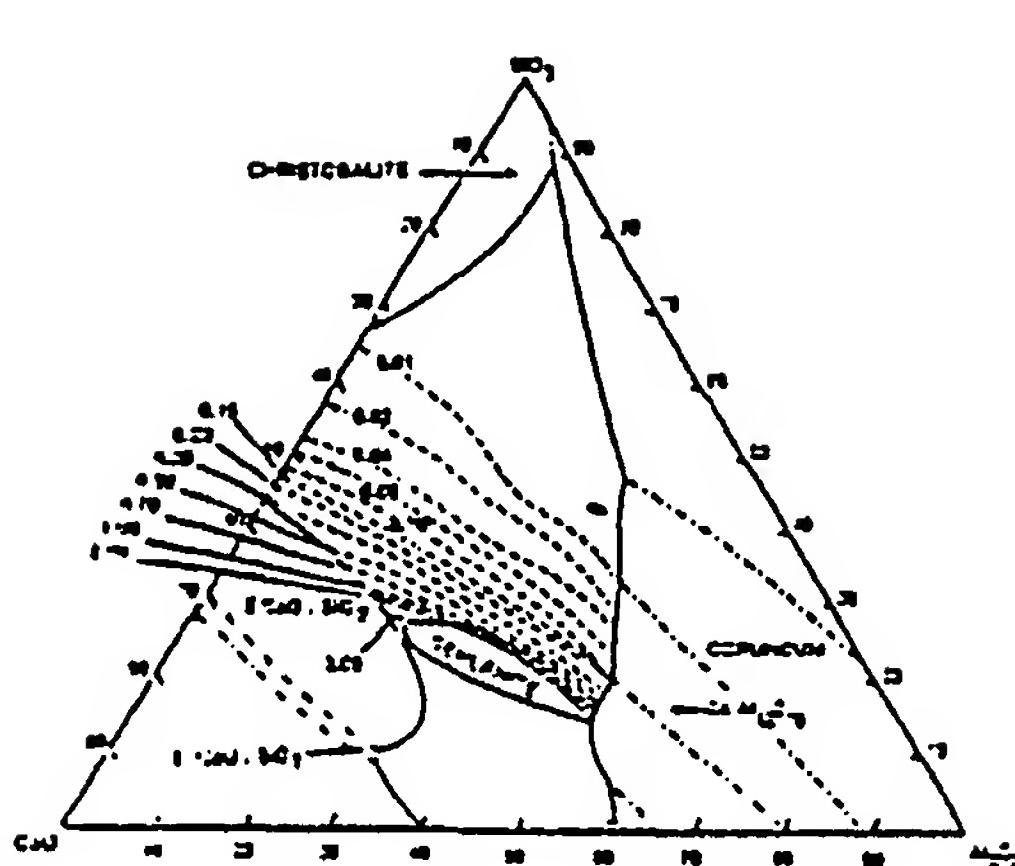


Fig.1 Isoconcentrational lines for Ca in Fe75Si-alloys in equilibrium with CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> slags at 1550°C. Concentrations in weight % /1/

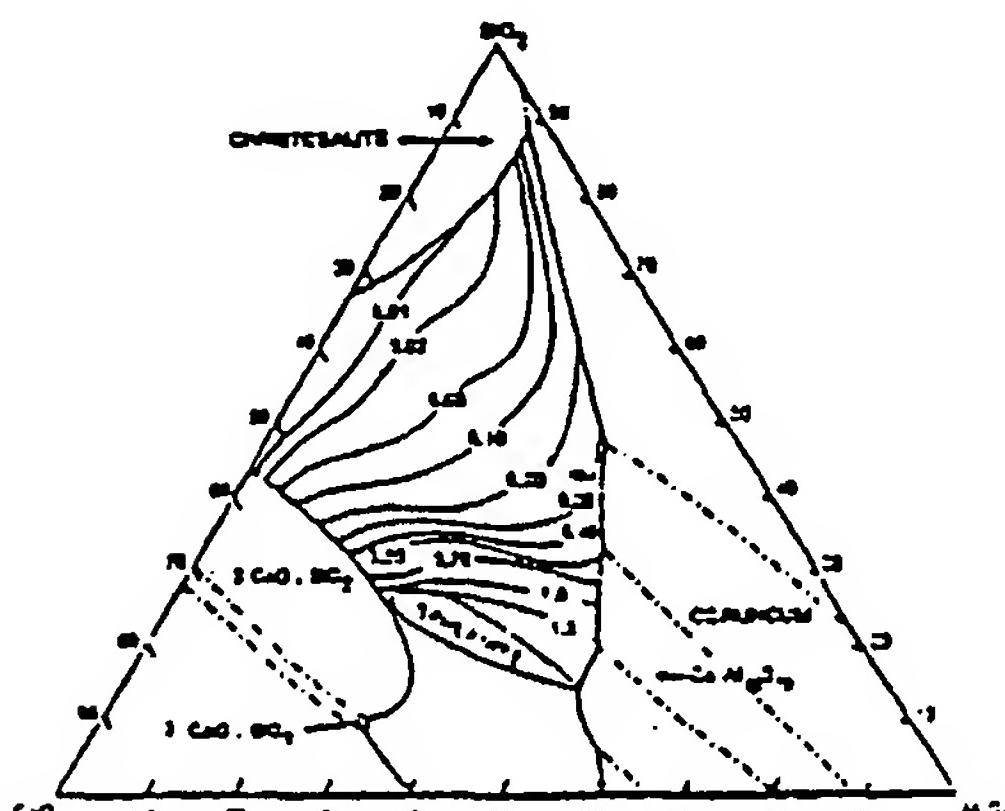


Fig.2 Isoconcentrational lines for Al in Fe75Si-alloys in equilibrium with CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> slags at 1550°C. Concentrations in weight % /1/

When the data in these diagrams are applied for silicon metal in equilibrium with the same slags, the impurity concentrations have to be corrected relative to the given values for ferrosilicon as follows<sup>11</sup>

$$[\%Ca]_{Si} = 1.26 [\%Ca]_{FeSi} \frac{\gamma_{Ca}^{FeSi}}{\gamma_{Ca}^Si} \quad (6)$$

$$[\%Al]_{Si} = 1.32 [\%Al]_{FeSi} \frac{\gamma_{Al}^{FeSi}}{\gamma_{Al}^Si} \quad (7)$$

The constant factors appearing in these expressions are dominated by the change in silicon activity as we are going from ferrosilicon to an iron-free system, but they are in principle valid only for impurity levels close to infinite dilution. A corresponding change will also appear in the activity coefficients of calcium and aluminium respectively, as expressed in terms of  $\gamma$ -ratios. Owing to the stronger interaction between the iron and silicon than that between the iron and dissolved impurities, these ratios are both expected to be greater than unity.

For calcium, the following corrections have been proposed<sup>12</sup>:

$$\frac{\gamma_{Ca}^{FeSi}}{\gamma_{Ca}^Si} = \frac{2.1 \cdot 10^{-3}}{8 \cdot 10^{-4}} = 2.6 \quad (8)$$

$$\Rightarrow [\%Ca]_{Si} = 3.2 [\%Ca]_{FeSi}$$

Inserting the value 0.006% as the concentration of calcium in ferrosilicon in equilibrium with an alumina-free silica-saturated slag, yields 0.02% Ca as the equilibrium concentration in silicon. This agree fairly well with values obtained at 1550°C in ongoing experimental work carried at our laboratories at SINTEF/NTH.

For silicon in presence of solid silica and mullite in a CaO-free system, we have arrived to 0.33% Al as the equilibrium concentration of aluminium at 1550°C. This yields  $\gamma_{Al}^Si = 0.19$ . This value combined with the value of 0.45 as previously derived for aluminium in

"ferrosilicon", the corrections for aluminium will be as follows:

$$\frac{\gamma_{Al}^{F, Si}}{\gamma_{Al}^{Si}} = \frac{0.45}{0.19} = 2.4 \quad (9)$$

$$\Rightarrow [\% Al]_{Si} = 3.1 [\% Al]_{F, Si}$$

### EQUILIBRIUM REACTION PATHS AND THEIR KINETICAL INTERPRETATIONS

In silicon refining, the density of the slags formed is nearly the same as that for the metal. Figure 3 shows the density for some compositions of slags in the system  $CaO-Al_2O_3-SiO_2$  at  $1500^{\circ}C$ . Remembering now that liquid silicon at this temperature has a density of  $2.50 \text{ g/cm}^3$ , it becomes clear that the silica-rich slags of this type will float on silicon, whereas the more basic and alumina rich slags tend to sink.

The viscosity is another property of the slags that counts in silicon metal refining; its variation with composition at  $1500^{\circ}C$  is as shown by isoviscosity lines in Figure 4.

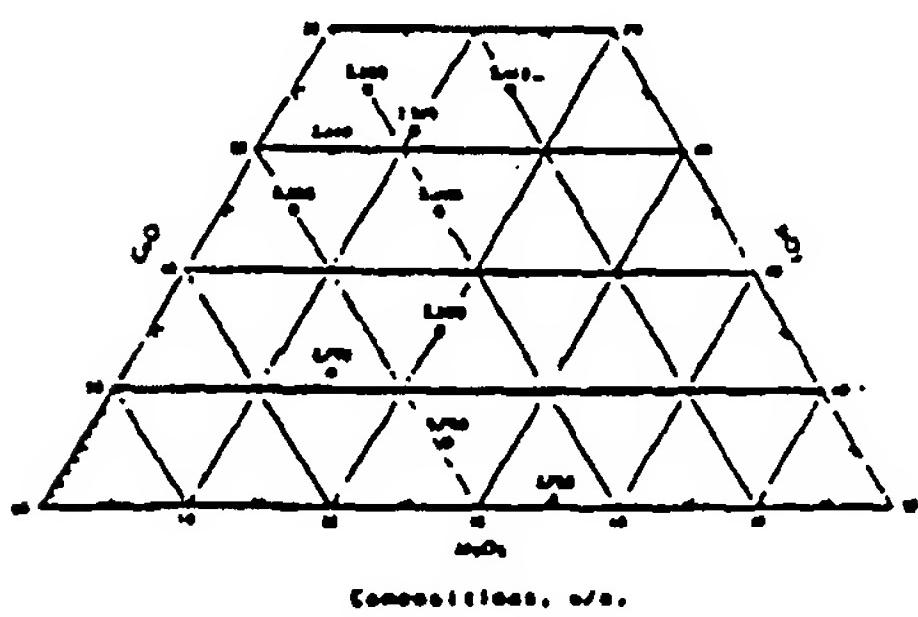


Fig.3 Density ( $\text{g/cm}^3$ ) for some compositions of  $CaO-SiO_2-Al_2O_3$  slags at  $1500^{\circ}C$  from /11/

Based on the distribution data for Ca and Al presented, which are superimposed on one diagram in Figure

5 and corrected for the transition from ferrosilicon to silicon, we shall now discuss what happens when silicon metal containing 0.20% Ca and 0.62% Al is blown with an oxygen bearing gas at  $1550^{\circ}C$ . Assuming then that a boundary slag layer forms at the metal/gas interface of the gas bubbles being created deep in the ladle, and that this slag reaches equilibrium with the bulk metal before the bubbles burst at the surface, leaving their slag content behind. The composition of the slag formed in the initial stage of the refining process is then as indicated by the letter A in Figure 5 where a fully and heavily drawn straight line marks the distinction between sinking and floating slags at  $1500^{\circ}C$ . This slag, which is fluid and tends to sink in silicon, has a calcium-to-aluminium ratio larger than that of the metal. Consequently, the metal becomes depleted in calcium. Nearly independent on whether the initially formed slag participates in the further reaction or not, the product slag changes its composition from A towards B in Figure 5 as the metal changes its composition from 0.6 to 0.45 per cent aluminium and from 0.2 to less than 0.03 per cent calcium.

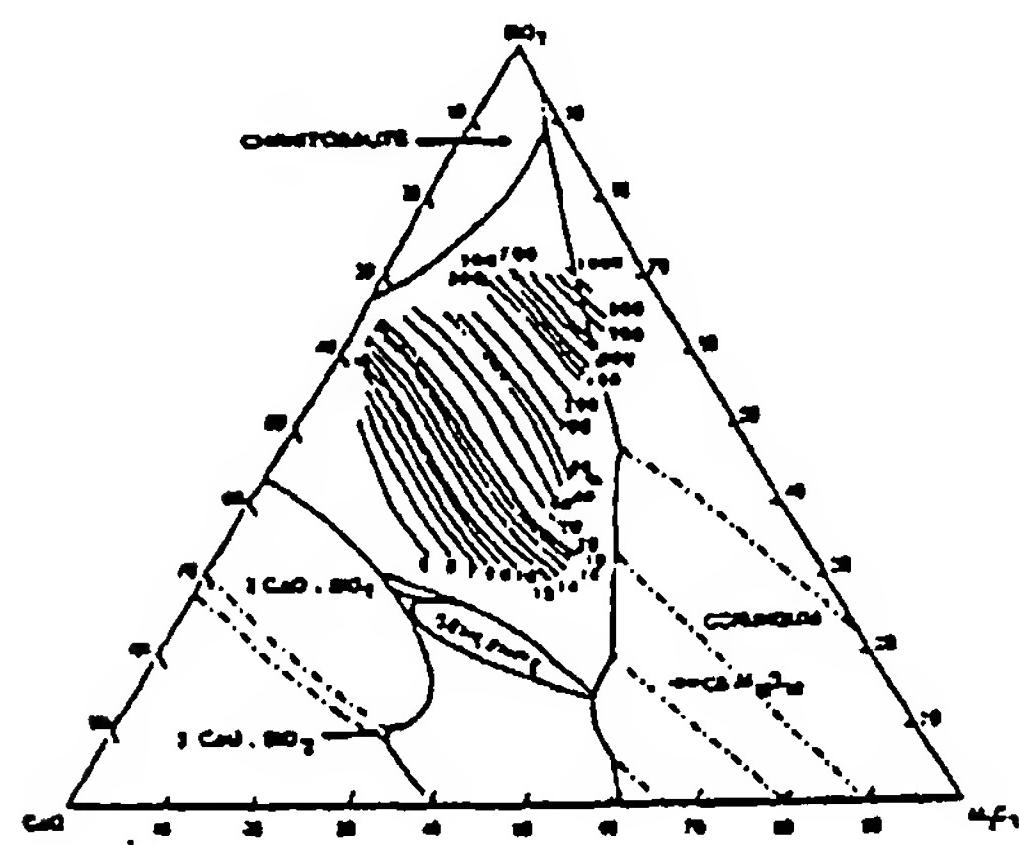
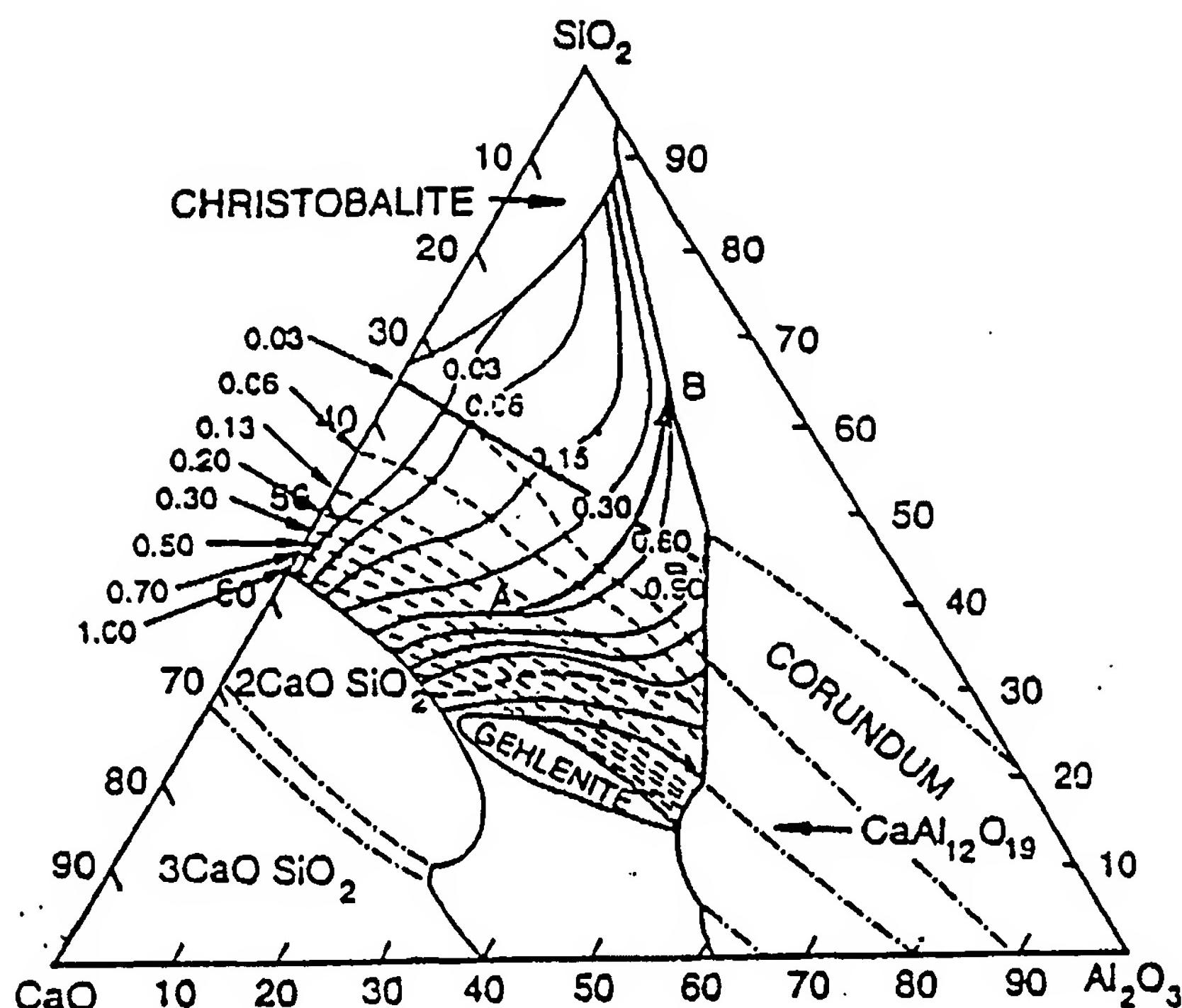


Fig.4 Isoviscosity lines (poise) in the  $CaO-SiO_2-Al_2O_3$  system at  $1500^{\circ}C$  redrawn from data in /11/



**Fig.5** Isoconcentrational lines for Ca (dashed lines) and Al (solid lines) in Fe75Si at 1550°C as reproduced from Figs 1 and 2, but corrected for transition to silicon. Path A-B represent change in product slag composition when silicon with 0.6% Al and 0.2% Ca reacts to equilibrium with oxygen. The heavy solid line represent a slag density of 2.5 g/cm<sup>2</sup> at 1500°C.

Along this path from A to B, the slag changes from being a free flowing sinking type to a none flowing floating type. For the removal of aluminum to continue beyond the above limit a highly viscous and partly solidified aluminasilicate slag has to form. One will therefore expect that the efficiency of oxidation process will decrease gradually as the calcium concentration of metal decreases, and that the aluminum content will tend to level off at a higher concentration than predicted for a fully silicon-saturated slag.

This agrees with observations made during industrial trials and bench scale testing. The process is running with nearly 100% oxygen utilization in the initial stage when calcium is present and a liquid slag is formed, but becomes inefficient as soon as the calcium is

consumed and a crusty, nearly dry oxidation product of aluminasilicates starts to form.

Deficiency of calcium at the site of oxidation will not only influence on the oxygen yield as described, but will also have a dramatic effect on analyzed oxygen in the product metal, owing to the formation of crusty aluminasilicate films that do not easily dissolve or separate from the liquid metal. Such tiny particles, being difficult to identify in the microscope, will, of course, result in oxygen levels far in excess of the liquid solubility values.

If oxygen lancing is used and the degree of mixing is limited, the flux should preferably be injected with the oxygen. This is, however, not necessary in an air/oxygen-blown process using a bottom plug as described for the Tinject

process 3, where the top slag appears to participate in the reaction throughout due to intimate mixing. In this case direct addition of flux to the surface of the metal is sufficient.

### OXYGEN IN REFINED SILICON

Oxygen is present in the liquid metal both as dissolved oxygen ( $O$ ) and in the form of suspended slag droplets or crusty  $Al_2O_3$ - $SiO_2$ -rich films.

The solubility of oxygen in silicon has been studied by a number of investigators, most recently by Hirata and Hoshikawa <sup>4</sup>, who equilibrated electronic grade silicon with  $SiO_2$  in evacuated ampullaes of fused silica. The ampullaes, which were contained in small graphite crucibles, were fairly rapidly cooled and the encapsulation of silica was removed by HF-etching. The metal was then crushed to 3-4 mm grains which were etched before they were analyzed on oxygen by use of the IGF method. We are using the same technique, but have in addition used a crucible method, where charges of about 1 kg of Wacker silicon are melted in open silica crucibles under a protective atm. of argon, and where metal samples are drawn and rapidly quenched by use of a Taylor pipette.

Some preliminary results of our investigations on the binary system Si-O are shown in Figure 6 together with data of Novokhatkiy et al. <sup>5</sup>, Hirata and Hoshikawa <sup>4</sup> for the liquid range, and the data of Wriedt <sup>6</sup> for the solid range.

As seen, our results appear to give oxygen solubilities which are even lower than those of Hirata and Hoshikawa, and, of course, very much lower than those of Novokhatkiy. This is in particular the case for the open crucible experiments where losses of oxygen due to  $SiO_2$ -evaporation may explain that saturation has not been achieved.

Accepting now that the oxygen solubility in pure silicon is low, less than 40 ppm  $O$  at 1500°C, there are reasons to ask if this is also the case when impurities of calcium and aluminium are present. These elements are both known to interact quite strongly with dissolved oxygen in metals being more noble than themselves, and this is reflected in their interaction coefficients being negative, i.e.  $\epsilon_O^Y < 0$ .

Aluminium, in particular, is therefore expected to increase the solubility of oxygen in silicon provided the oxygen activity remains constant, as is the case in a silica-saturated system. This is confirmed experimentally as shown in Figure 7.

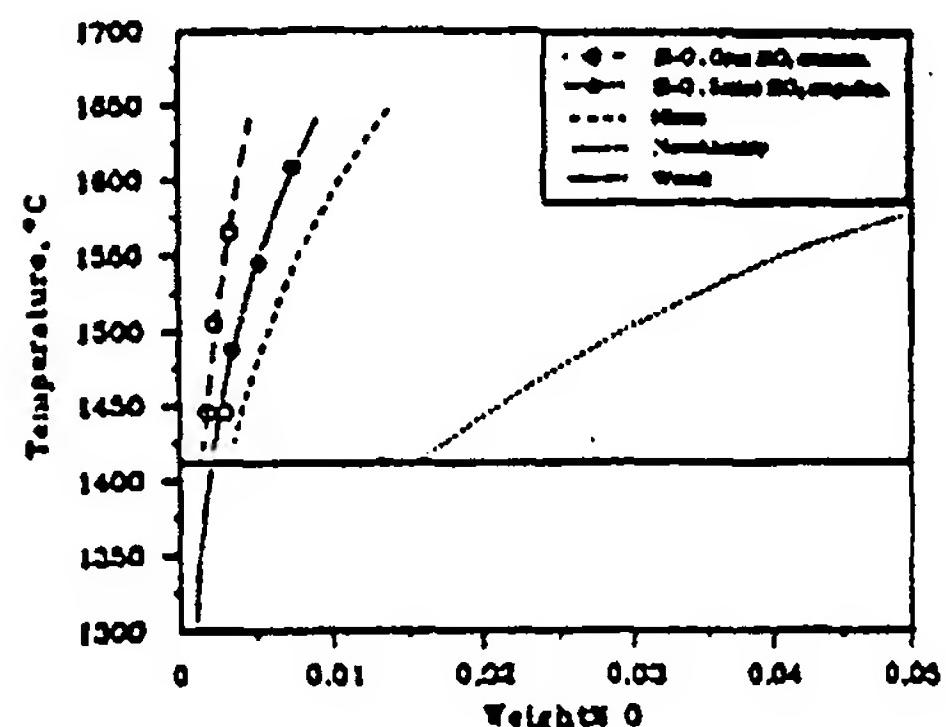


Fig.6 Solubility of oxygen in solid and liquid silicon-experimental results.

The effect of calcium, on the other hand, is more difficult to predict because it interacts with both the oxygen and the silicon. Our preliminary results with calcium added in the form of wollastonite, which are shown in Figure 8, are unfortunately not quite conclusive on that point, but they indicate a slight increase in dissolved oxygen even for a situation where the saturation on silica may be questioned.

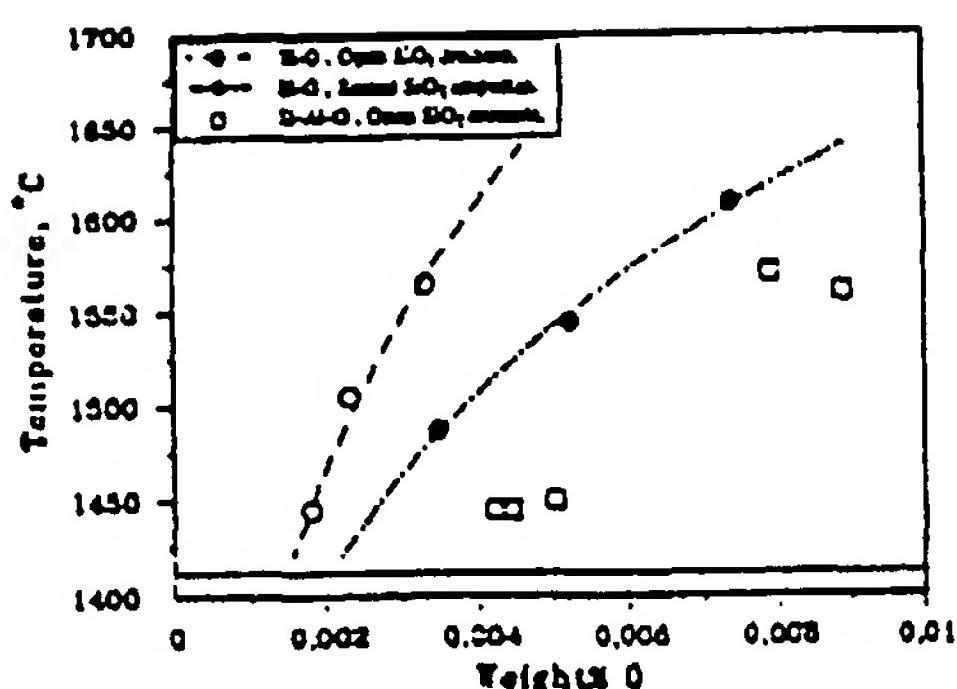


Fig.7 Effect of aluminium on the solubility of oxygen in liquid silicon at silica-saturation. Preliminary results.

Due to the uncertainties attached to the open crucible experiments regarding the question of saturation, we are not, at the present time able to derive reliable values for the interaction parameters of these elements on oxygen. Such values are needed in order to see what happens to the content of dissolved oxygen in a metal equilibrated with unsaturated slags. The oxygen activity of the system decreases as the silica activity decreases, but decrease in the activity coefficient of the dissolved oxygen due to increasing concentrations of aluminium may more than compensate for this. Further work is therefore needed on these systems, but it seems fair to say already, that oxygen levels in excess of 60-70 ppm in refined metal are caused by the presence of suspended oxides.

#### CARBON IN LIQUID SILICON

In the reduction furnace, silicon forms in presence of silicon carbide at temperatures in the range 1800 to 2000°C. The carbon content of tapped metal therefore reflects the solubility of carbon in silicon at these temperatures, but will be found as silicon carbide inclusions in the solidified metal. This is clear from the portion of the phase diagram of the Si-C system shown in

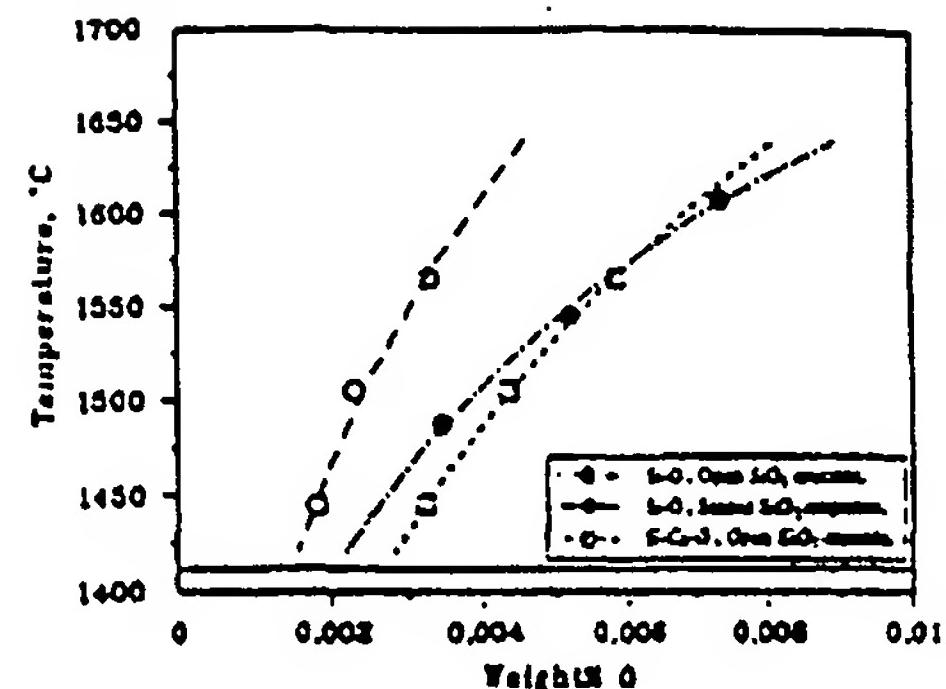


Fig.8 Effect of calcium on the oxygen solubility in liquid silicon, preliminary result with wollastonite additions.

Figure 9, where the liquid solubility curve has been drawn on basis of the work of Scace and Slack<sup>7</sup>, and where an enlarged portion near the melting point of silicon, as given by Nozaki et al.<sup>8</sup>, has been included in order to show the eutectic nature of the system.

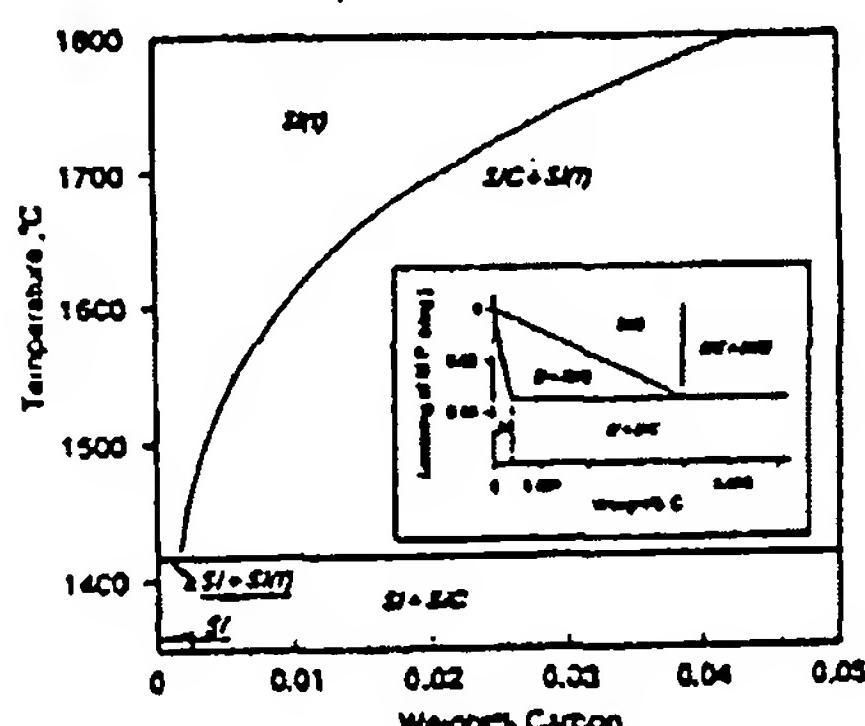


Fig.9 Solubility of C in liquid Si derived from data of Scace and Slack<sup>7/1</sup> including the eutectic portion of the Si-C system as given by Nozaki et al.<sup>8/1</sup>.

A more recent publication by Oden and McCune<sup>9</sup> indicates, however, a lower liquid solubility than given in Figure 9, whereas the older data of Hall<sup>10</sup> are significantly higher. In order to check this discrepancy, we decided to make a

series of experiments using the set up shown in Figure 10, where the Taylor pipette used for sampling is placed in an operative position in one of the crucibles. The quenched samples were ground in an agate mortar and analyzed at Elkem Research by use of a Leco carbon/sulphur determinator. The results obtained are plotted in Figure 11 where they are compared with solubility curves derived from the publications already referred to.

As seen, the present results are in good agreement with the data of Hall at low temperatures but deviates at higher temperatures.

Strictly speaking, it is worth noticing that our system is not a purely binary system, but rather a part of the ternary system Si-C-O, where the oxygen potential has not been defined. We do not believe, however, that the presence of oxygen will effect the oxygen solubility significantly, and in case it does, the oxygen will rather decrease the carbon solubility than to increase it.

Experiments have also shown that the presence of iron decreases the carbon solubility slightly. The same is expected for the presence of calcium. Aluminum, on the other hand, increases the carbon solubility in liquid silicon<sup>9</sup>.

Apart from these effects, the carbon is hardly not affected chemically in the oxidative refining of the metal. Nevertheless, some carbon, being present as suspended silicon carbide particles in the metal, is actually removed during the process. This is the result of a physical separation process where differences in densities and interfacial energies together with the degree of turbulence in the system, are factors of importance.

Silicon carbide with a density of 3.05 g/cm<sup>3</sup> tend to sink in both liquid silicon and slag. It is also a fact that the slag wets silicon carbide better than it does

the metal. The extent to which suspended particles of silicon carbide can be effectively removed in an oxidative refining process therefore depends primarily on the fluidity of the slag, the degree of intermixing of metal and slag, as well as on conditions under which the phases separate.

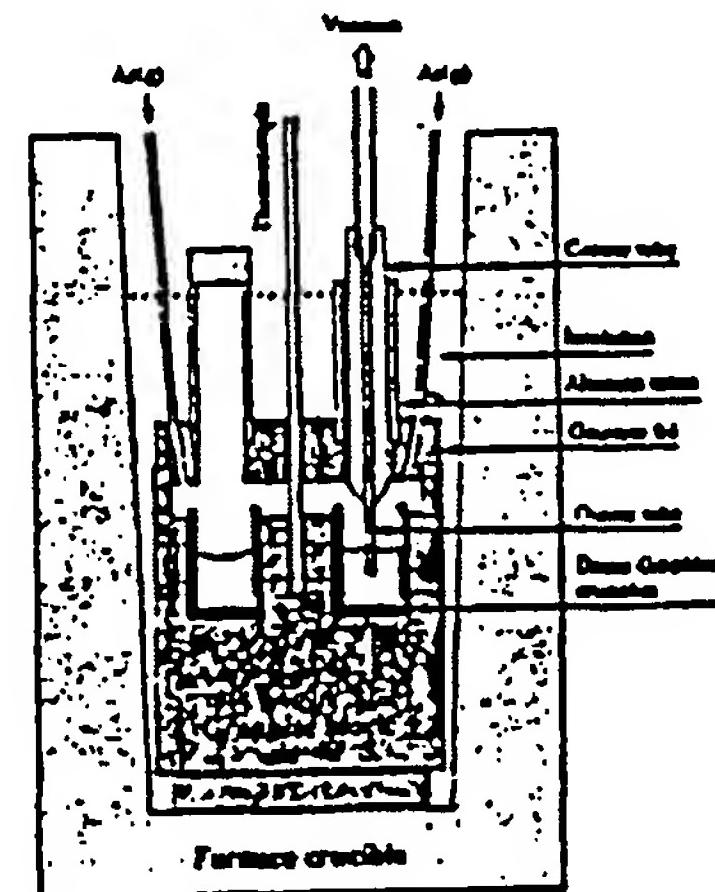


Fig.10 Experimental setup and sampling technique used for determination of carbon solubilities.

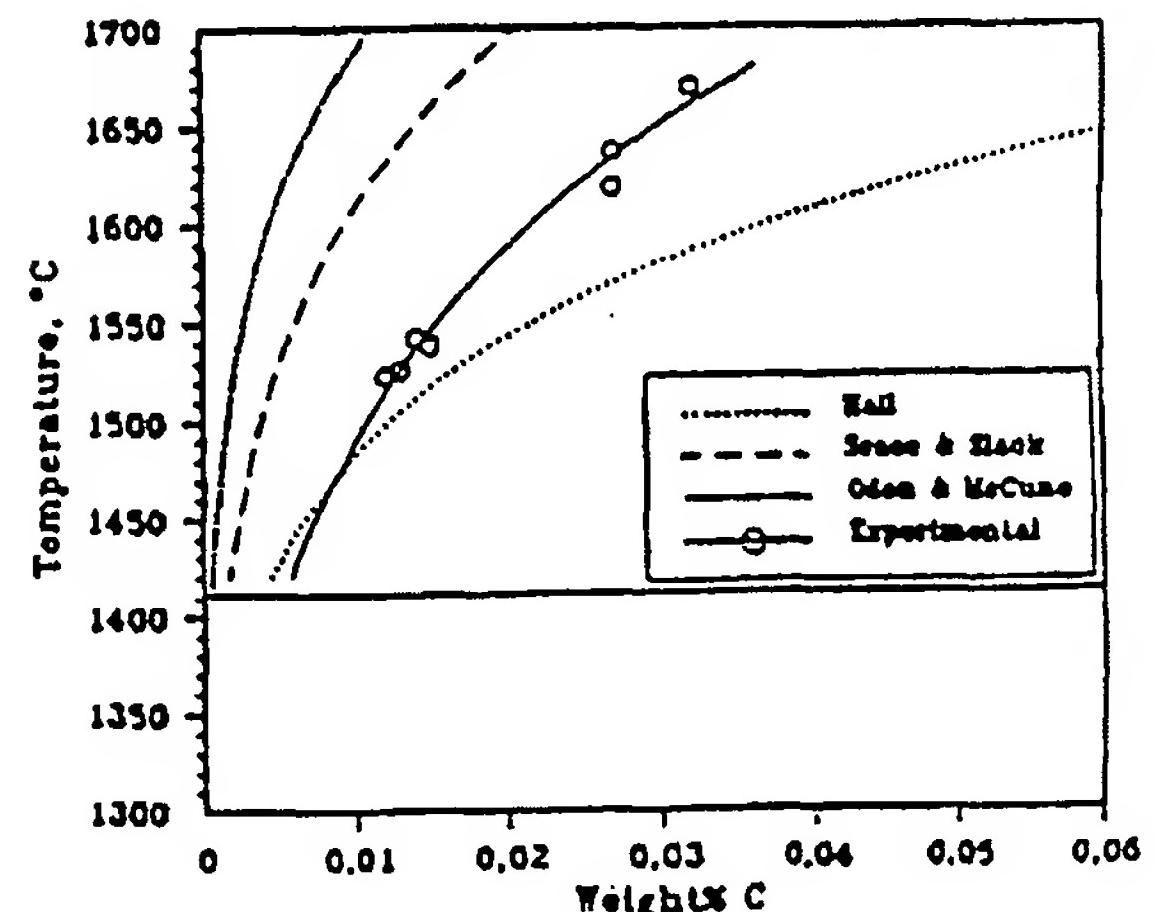


Fig.11 Carbon solubilities in liquid silicon, preliminary experimental results.

## CONCLUDING REMARKS

The purpose of this presentation has been to review our present knowledge and understanding of the fundamentals of the oxidative process for refining of silicon metal. It has also been considered to be of importance to point out where we still have to rely upon questimates instead of knowledge, and where further work is needed.

## ACKNOWLEDGEMENT

The authors gratefully acknowledge the financial support from the Research Association of the Norwegian Ferroalloy Producers (FFF) and the Royal Norwegian Council for Scientific and Industrial Research (NTNF).

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**EXHIBIT B**

sociated with the overaging of precipitation-hardened materials. Although noticeable coarsening of thorium particles occurred, this was not strongly reflected in the short-time tensile strength.

The introduction of cold work by swaging increased elevated- and room-temperature strength. After annealing at 2500°F the strengthening was still retained at 2000°F, but not at room temperature. The strength at room temperature appears much more affected by annealing treatments than at elevated temperatures. Mechanistically undefined recovery processes affecting strength, hardness, and X-ray line breadth were noted at temperatures as low as 1000°F, but these processes do not appear to have a strong effect on elevated-temperature strength.

In swaged or as-received form TD Nickel bar could not be recrystallized after anneals up to 2500°F. Comparable reductions by rolling, however, resulted in a coarse-grain recrystallized structure upon subsequent heat treatment. The reason for this variation in response for different working operations was not established. The tensile strength of the recrystallized material was not appreciably lower than that of the cold-worked material.

The elevated-temperature tensile strength in as-

received bar stock was anisotropic above 550°F, the longitudinal strength exceeding the transverse strength by a factor of five. The anisotropy has the following characteristics.

- 1) The strength difference at 2000°F is related to the prior processing of the bar, with the difference increasing with increasing accumulated deformation.
- 2) The variation in strength is also related to the direction of metal flow and appears to partially reverse when the flow direction is reversed.
- 3) The difference in tensile strength between longitudinal and transverse direction varies with test temperature and is not obtained below one third the absolute melting point for the strain rates of this investigation.
- 4) The initiation of the divergence and magnitude of the strength difference depend upon strain rate.

No explanation for the mechanism of the anisotropy is advanced.

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# Activities in the Liquid Solution $\text{SiO}_2\text{-CaO-MgO-Al}_2\text{O}_3$ at 1600°C

Richard H. Rein and John Chipman

The activity of  $\text{SiO}_2$  in the entire liquid system  $\text{SiO}_2\text{-CaO-MgO-Al}_2\text{O}_3$  at 1600°C is calculated from the distribution of silicon between these slags and Fe-Si-C alloys saturated with either graphite or silicon carbide, the activity coefficient of silicon in these alloys, and the requisite thermodynamic data. The activities of the other components in the ternary systems  $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3$ ,  $\text{SiO}_2\text{-MgO-CaO}$ ,  $\text{SiO}_2\text{-MgO-Al}_2\text{O}_3$  are computed from these data by the

IRON blast-furnace slags can be regarded as consisting of the four major oxide components,  $\text{SiO}_2$ ,  $\text{CaO}$ ,  $\text{MgO}$ , and  $\text{Al}_2\text{O}_3$  along with minor proportions of other oxides and of sulfur. The purpose of this study is to measure the activity of silica in the liquid solutions of these four oxides at iron-making

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Gibbs-Duhem equation with the aid of the known free energies of several of the interoxide compounds and the accepted phase diagrams. Based on these activities, new data are presented for the free energy of formation of a number of the interoxide compounds. The free energy of mixing the liquid metasilicates of  $\text{CaO}$  and  $\text{MgO}$  shows slight positive deviations from the ideal.

temperatures and to obtain activities of the other components by application of the Gibbs-Duhem equation and the properties of several interoxide compounds.

Recent investigations on the activity of silica in the  $\text{SiO}_2\text{-CaO-Al}_2\text{O}_3$  system<sup>1-3</sup> and recognition of a serious error in older data for the free energy of formation of  $\text{SiO}_2$  (Ref. 4) have succeeded in bringing a fair degree of concordance into the results of different investigators. In the present study, the activity of silica is obtained from the silicon-distribution experiments described in a previous paper,<sup>5</sup> the revised activity coefficient of silicon

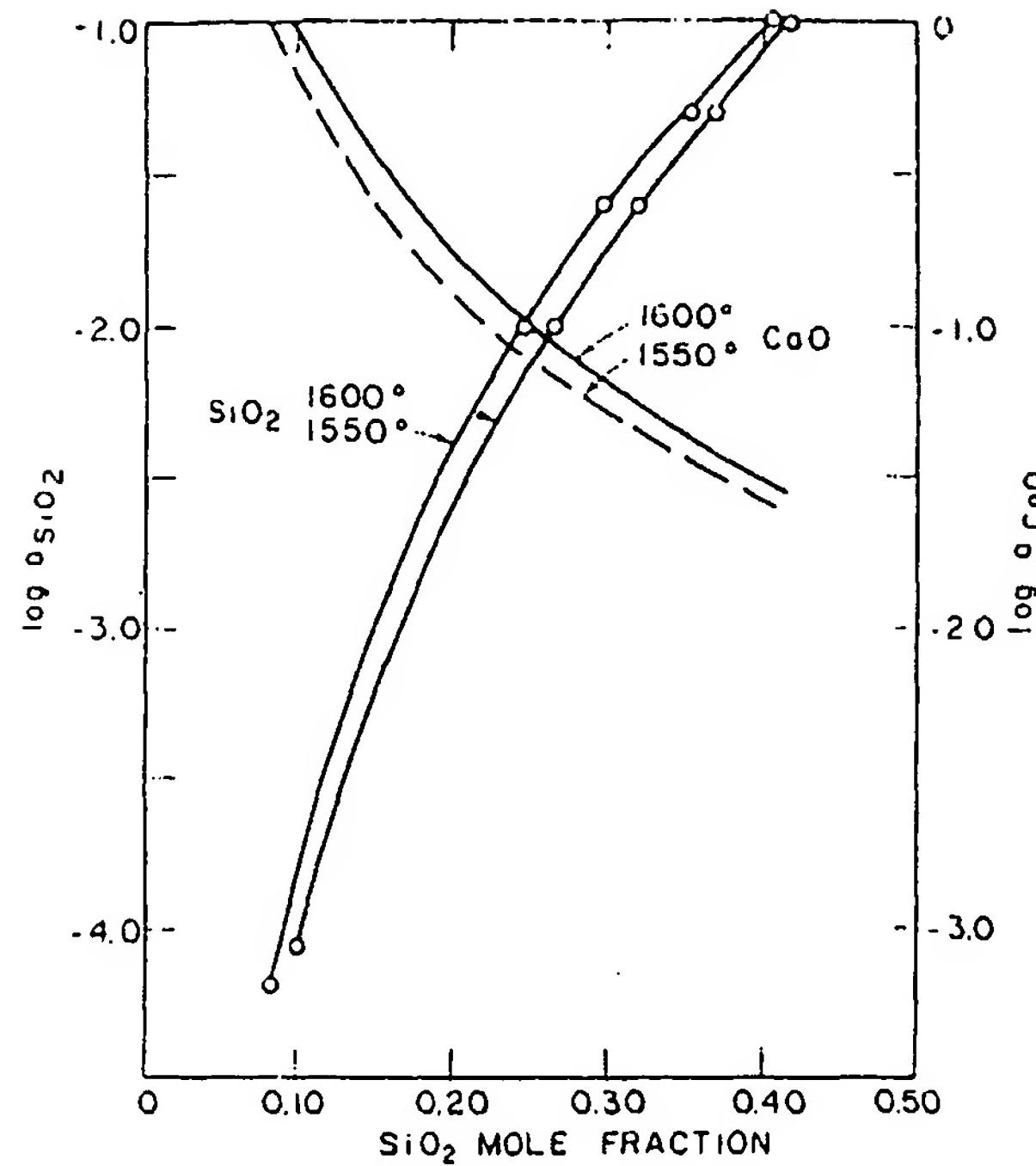


Fig. 6—Activities of  $\text{SiO}_2$  and  $\text{CaO}$  in slags saturated with dicalcium silicate.

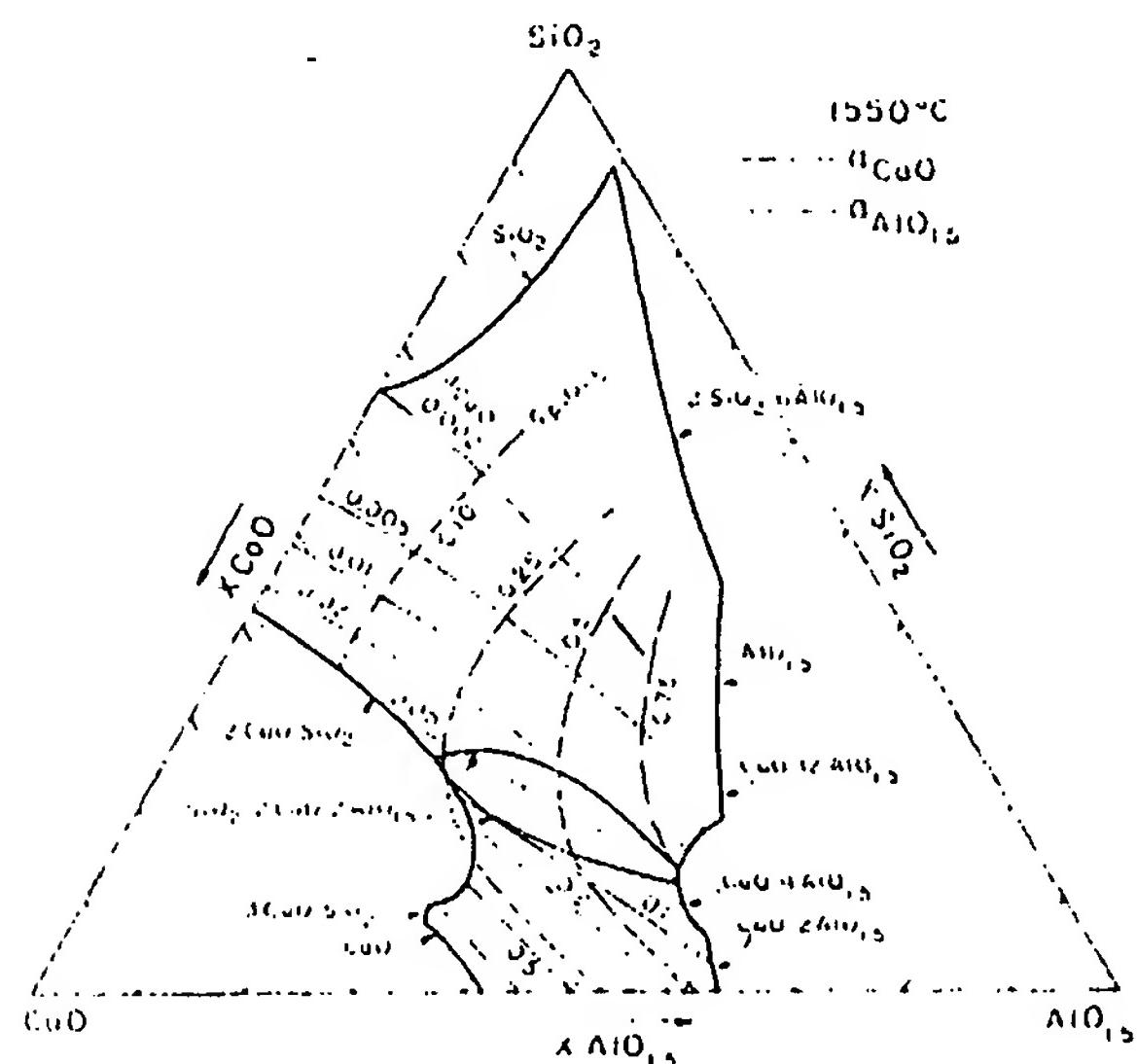


Fig. 7—Activities of  $\text{CaO}$  and  $\text{Al}_2\text{O}_3$  in  $\text{SiO}_2\text{-CaO}\text{-Al}_2\text{O}_3$  slags at  $1550^\circ\text{C}$ .

activities within the favorable experimental range and extending the curve to the dicalcium silicate-line saturation using the values calculated above. These data are shown in Fig. 6. The activity of lime along this isotherm is calculated from the silica activities and the equilibrium constant. The lower isoactivity lines for  $\text{SiO}_2$  were based on this curve and on the free energy of gehlenite discussed in the section on interoxide compounds.

The activities of  $\text{CaO}$  and  $\text{Al}_2\text{O}_3$  were calculated from the  $\text{SiO}_2$  activities using the method of Schuh-

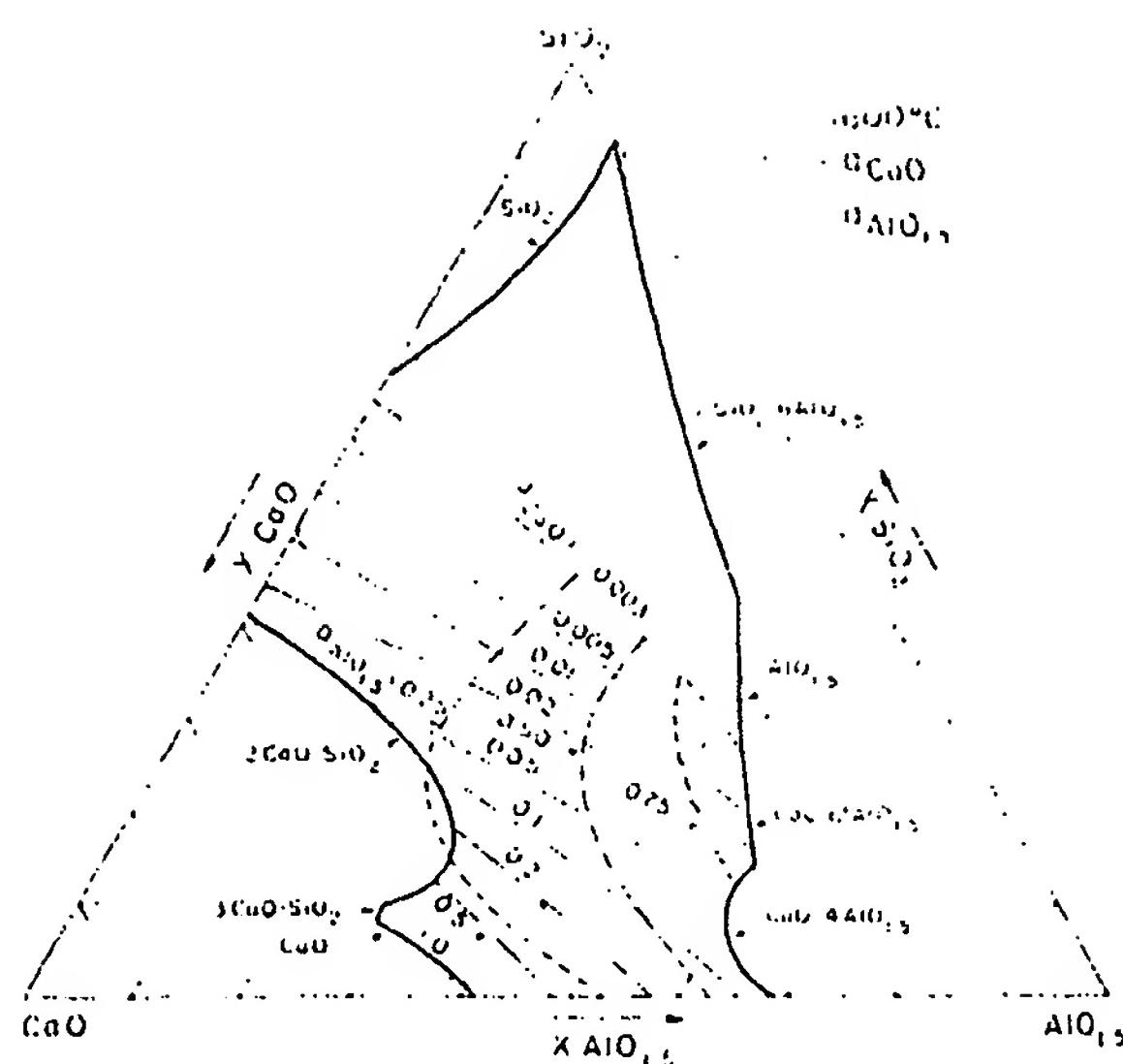


Fig. 8—Activities of  $\text{CaO}$  and  $\text{Al}_2\text{O}_3$  in  $\text{SiO}_2\text{-CaO}\text{-Al}_2\text{O}_3$  slags at  $1600^\circ\text{C}$ .

mann<sup>30</sup> which is particularly suited to this type of analysis. Activities in the binary system shown in Fig. 3 were taken as the starting points. The computations were aided by data on the free energies of several of the interoxide compounds as discussed in the following section. The results are shown in Figs. 7 and 8.

#### COMPOUNDS OF THE SYSTEM $\text{SiO}_2\text{-CaO}\text{-Al}_2\text{O}_3$

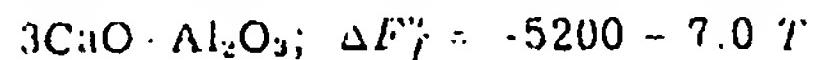
The free energies of formation of several binary compounds from their constituent oxides have already been discussed and are listed in Table I. Several others, including ternary compounds, have been found useful in fixing the activity lines, and in a few instances the activity data provide values of the free energy which may be compared with the results of thermochemical investigations. These are discussed in this section and the appropriate equations are entered in Table I.

The free energy of formation of mullite ( $2\text{SiO}_2 \cdot 3\text{Al}_2\text{O}_5$ ) can be obtained by interpolation to find the activity of  $\text{SiO}_2$  in equilibrium with slags saturated with mullite and alumina. Referring to Figs. 4 and 5, this is equal to 0.47 at  $1550^\circ\text{C}$  and 0.44 at  $1600^\circ\text{C}$  and gives  $\Delta F''_{\text{rea}} = +5.5$  kcal and  $\Delta F''_{\text{rea}} = +6.1$  kcal. To establish this point more definitely two additional experiments were carried out at  $1550^\circ\text{C}$ . In both cases the slag was saturated both with alumina and with mullite. The data on these two experiments are shown in Table III.

Table III. Equilibrium with  $\text{Al}_2\text{O}_3$  and Mullite at  $1550^\circ\text{C}$

Run No.	Initial		Final		$\Delta S_f$	$\Delta C_f$	$a_{\text{SiO}_2}$
	wt % Si	wt % Si	wt % C	wt % Al <sub>2</sub> O <sub>3</sub>			
85-1	20.0	20.5	0.45	0.972	0.335	0.018	0.0286
85-2	21.0	21.0	0.45	0.972	0.341	0.017	0.0306

the other data, the thermochemical values require a correction of -2.2 kcal. Since neither  $\Delta H$  nor  $\Delta S$  appears to be so much in error, the correction is divided between them to yield the equation:



The heat of fusion of this compound may be estimated very roughly as 39.8 kcal, corresponding to an entropy of fusion of 22.0. The free energy of formation of the liquid at this composition is, therefore,  $+34,600 - 29.0 T$ . Having drawn in the upper portions of the lines for activity of CaO, this permits calculation of the activity of  $\text{AlO}_{1.5}$  at this composition, shown in the points *g* and *h* for 1600° and 1700°C, respectively.

On the other side of the diagram, the thermochemical value for the free energy of the compound  $\text{CaO} \cdot 2\text{Al}_2\text{O}_5$  involves a considerable uncertainty in its heat of formation. Its solubility at 1600° and 1700°C can be read from the phase diagram, and its free energy of formation can be calculated from the activity data. The result is a value more negative than that of Kochler, Barany, and Kelley by about 3 kcal. Retaining their value for the entropy change, its free energy of formation may be represented by the equation:



Since the calculation involves extrapolation both in temperature and in composition, the result is probably not better than  $\pm 2$  kcal.

In this treatment of the binary system we have adopted the free energies of two of the four compounds investigated by Kelley and coworkers and have suggested substantial correction for the two end members of the series. This should not be taken to mean that the results of Sharma and Richardson confirm the values for the two central members and contradict those for the other two.

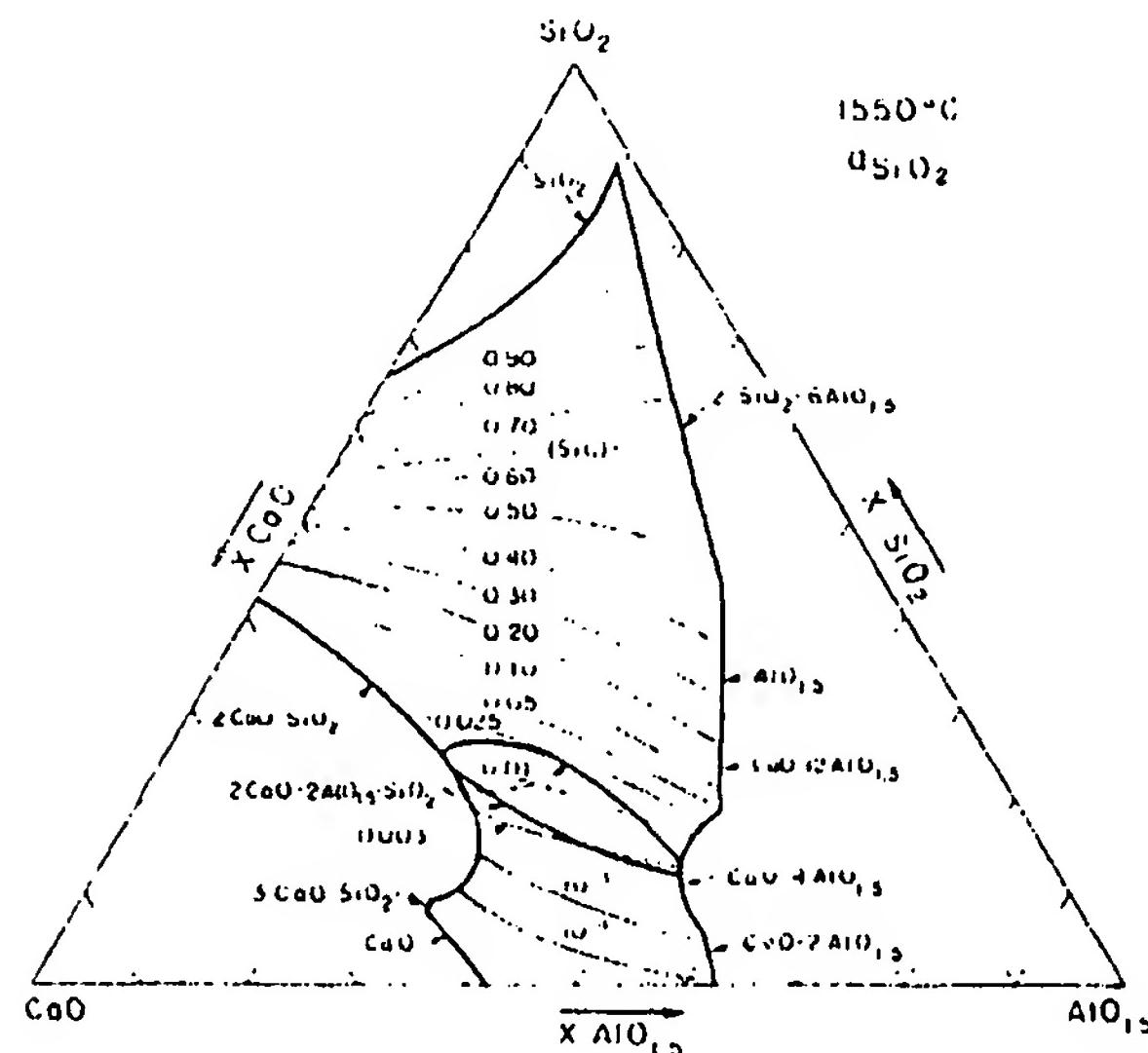


Fig. 4—Activity of  $\text{SiO}_2$  in  $\text{SiO}_2\text{-CaO}\text{-Al}_2\text{O}_5$  slags at 1550°C.

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It means readily that, when considered in the light of the activity data, the free energies of the two central members derived from thermochemistry are in remarkably good agreement with one another and not with the other two. Conceivably it would be possible to work out a satisfactory treatment of the data based on the two end members of the series, but until new thermochemical data become available this approach seems unwarranted.

### THE SYSTEM $\text{SiO}_2\text{-CaO}\text{-Al}_2\text{O}_5$

The activity of  $\text{SiO}_2$  is shown in Figs. 4 and 5. Assignment of the formula  $\text{AlO}_{1.5}$  to alumina gives results which are more readily correlated with ionic theories of slag constitution and produces diagrams more nearly resembling the familiar ones based on weight percent.

The curvature of the lines of constant silica activity is confirmed by the work of Kay and Taylor,<sup>1</sup> and the numerical values of the activity curves also agree within experimental error with these investigators. The slag composition at which  $\text{SiC}$  forms in the presence of 1 atm of CO is also indicated. This line will be shifted to higher silica compositions for CO pressures greater than 1 atm and to lower silica compositions for CO pressures less than 1 atm. At 1533°C the  $\text{SiC}$  line would coincide with the line of silica saturation.<sup>14</sup>

The activity of  $\text{SiO}_2$  in low-silica slags, where the distribution data are not well-defined, is obtained in the following manner. A point corresponding to saturation with both dicalcium silicate and lime can be determined by a slight extension of their solubility isotherms. The activity of  $\text{SiO}_2$  at this point is defined by the free energy of dicalcium silicate, since  $a_{\text{CaO}} = 1$ , from which  $a_{\text{SiO}_2} = 6.4 \times 10^{-6}$  at 1550°C and  $7.7 \times 10^{-6}$  at 1600°C. The activity of  $\text{SiO}_2$  along the entire dicalcium silicate isotherm was obtained by plotting the experimental silica

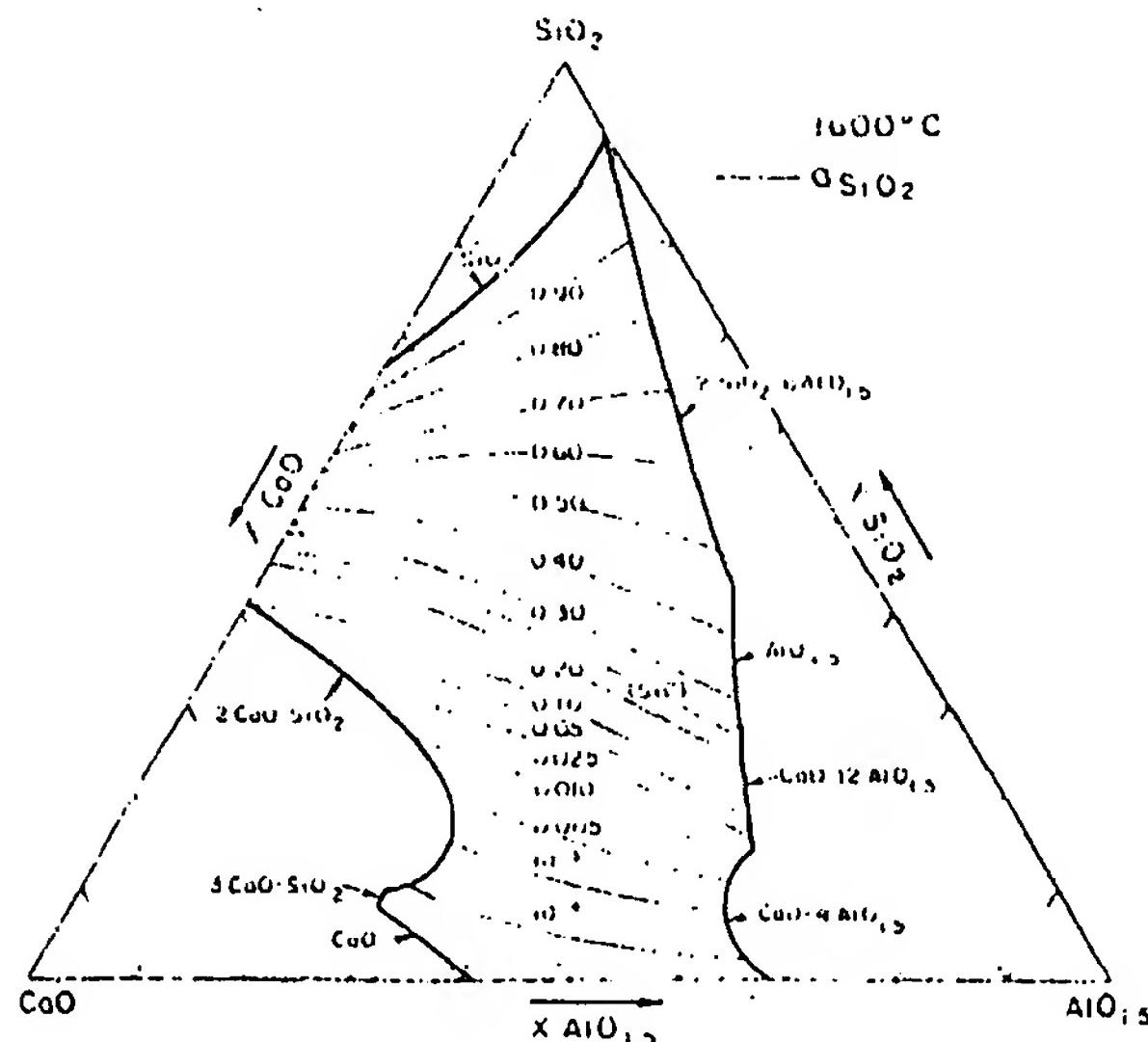


Fig. 5—Activity of  $\text{SiO}_2$  in  $\text{SiO}_2\text{-CaO}\text{-Al}_2\text{O}_5$  slags at 1600°C.

**EXHIBIT C**

# Critical Evaluation and Optimization of the Thermodynamic Properties and Phase Diagrams of the CaO-Al<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>, and CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> Systems

GUNNAR ERIKSSON and ARTHUR D. PELTON

All available thermodynamic and phase diagram data have been critically assessed for all phases in the CaO-Al<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>, and CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> systems at 1 bar pressure from 298 K to above the liquidus temperatures. All reliable data for the binary systems have been simultaneously optimized to obtain, for each system, one set of model equations for the Gibbs energy of the liquid slag and all solid phases as functions of composition and temperature. The modified quasichemical model was used for the slag. With these binary parameters and those from the optimization of the CaO-SiO<sub>2</sub> system reported previously, the quasichemical model was used to predict the thermodynamic properties of the ternary slag. Two additional small ternary parameters were required to reproduce the ternary phase diagram and ternary activity data to within experimental error limits. The calculated optimized phase diagram and thermodynamic properties are self-consistent and are the most reliable currently available estimates of the true values.

## I. INTRODUCTION

IN a thermodynamic "optimization," all available thermodynamic and phase equilibrium data for a system are evaluated simultaneously in order to obtain one set of model equations for the Gibbs energies of all phases as functions of temperature and composition. From these equations, all of the thermodynamic properties and the phase diagram can be back-calculated. In this way, all the data are rendered self-consistent and consistent with thermodynamic principles. Thermodynamic property data, such as activity data, can aid in the evaluation of the phase diagram, and phase diagram measurements can be used to deduce thermodynamic properties. Discrepancies in the available data can often be resolved, and interpolations and extrapolations can be made in a thermodynamically correct manner. A small set of model parameters is obtained. This is ideal for computer storage and calculation of properties and phase diagrams.

We are currently engaged in a systematic analysis of oxide systems with a view to developing a comprehensive database for molten and solid oxide phases for the system SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-CaO-MgO-MnO-FeO-Na<sub>2</sub>O-K<sub>2</sub>O-TiO<sub>2</sub>-Ti<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>-S. The first stage has been the optimization of all binary subsystems and is now completed. In a second stage, models are used to predict the thermodynamic properties of ternary solutions from the optimized model parameters of the constituent binaries. Ternary phase diagrams can be calculated from these estimated properties. The predictions are compared with measured ternary properties and phase diagrams, when these are available, and when necessary, small optimized ternary parameters are added. Finally, from the optimized binary and ternary parameters, thermodynamic properties and phase diagrams of multi-component systems can be predicted. The present article

reports on the evaluation of the CaO-Al<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> binary systems and the CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> ternary system. The optimization of the CaO-SiO<sub>2</sub> system was reported previously.<sup>11</sup>

For the molten slag phase, we have used our modified quasichemical model.<sup>12-13</sup> Details of the model have been given previously,<sup>12,41</sup> and the equations for binary systems have been summarized in a recent submission to this journal.<sup>11,41</sup> A brief outline of the model for a ternary system is given below. This includes, for the first time, a description of the inclusion of ternary terms. All temperatures in this article have been corrected to the International Temperature Scale of 1990.

## II. THE MODIFIED QUASICHEMICAL MODEL

In a molten slag AO<sub>x</sub>-BO<sub>y</sub>-CO<sub>z</sub>, we consider the formation of second nearest-neighbor (*i-j*) bonds from (*i-i*) and (*j-j*) bonds:

$$(A - A) + (B - B) = 2(A - B) \quad [1]$$

$$(B - B) + (C - C) = 2(B - C) \quad [2]$$

$$(C - C) + (A - A) = 2(C - A) \quad [3]$$

The Gibbs energy changes for these reactions are represented by ( $\omega_{AB} - \eta_{AB}T$ ), ( $\omega_{BC} - \eta_{BC}T$ ) and ( $\omega_{CA} - \eta_{CA}T$ ).

Let the mole fractions of the components be  $X_A = X_{AO_x}$ ,  $X_B = X_{BO_y}$ , and  $X_C = X_{CO_z}$ . Equivalent fractions are then defined as:

$$Y_A = b_A X_A / (b_A X_A + b_B X_B + b_C X_C) \quad [4]$$

and similarly for  $Y_B$  and  $Y_C$ , where  $b_A$ ,  $b_B$ , and  $b_C$  are constants. Letting  $X_{ij}$  be the fractions of each type of bond in solution, equilibrium constants are obtained for Reactions [1] through [3]:

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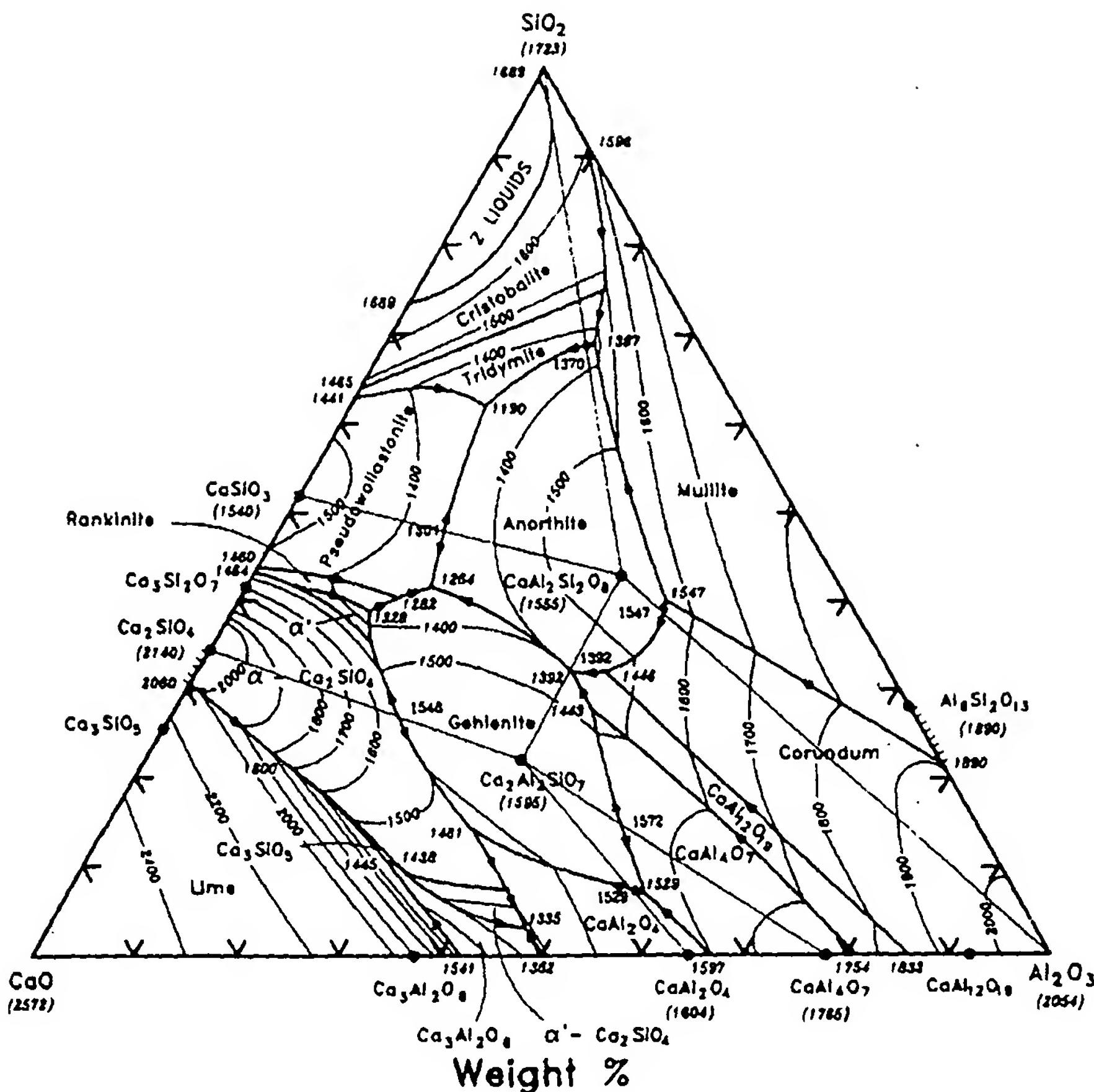


Fig. 5—Optimized CuO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> phase diagram. Temperature in °C.

$\text{SiO}_2 + 3\text{C} = \text{SiC} + 2\text{CO}$ . Results of Rein and Chipman at 1600 °C and of Kay and Taylor at 1550 °C are reproduced in Figures 6 and 7. The experiments of Rein and Chipman were repeated for very low SiO<sub>2</sub> activities by Ozturk and Fruehan,<sup>1711</sup> who obtained an isoactivity line for  $a_{\text{SiO}_2} = 10^{-4}$  at 1600 °C at SiO<sub>2</sub> contents about 3 wt pct higher than the line shown in Figure 6. Activities of CaO in the slag at 1500 °C were measured by Kalyanram *et al.*<sup>1721</sup> by gas/slag equilibration. Their results are reproduced in Figure 8.

Thermodynamic properties of anorthite (CaAl<sub>2</sub>Si<sub>2</sub>O<sub>7</sub>) and gehlenite (CaAl<sub>2</sub>SiO<sub>5</sub>) were taken from Berman and Brown.<sup>124,251</sup> The values of  $\Delta H_{298}^{\circ}$  for these compounds were subsequently adjusted by -2864 and +2299 J/mol in the optimization.

In order to reproduce the data within experimental error limits, two small ternary parameters were required in the quasichemical equations for the liquid. These were found by a nonlinear least-squares program written for that purpose.<sup>1171</sup> To the value of  $\omega_{\text{Ca-Si}}$  in the binary system from Eq. [17], the ternary term  $-88144 (Y_{\text{Al}_2\text{O}_3}/(Y_{\text{CaO}} + Y_{\text{Al}_2\text{O}_3}))^2$  J/mol was added. To the value of  $\omega_{\text{Al-Si}}$  in the binary system from Eq. [16], the ternary term  $-48668Y_{\text{CaO}}/(Y_{\text{CaO}} + Y_{\text{Al}_2\text{O}_3})$  J/mol was added. No ternary terms were required for  $\eta_{\text{Ca-Si}}$ ,  $\eta_{\text{Al-Si}}$ ,  $\omega_{\text{Ca-Al}}$ , or  $\eta_{\text{Ca-Al}}$ .

A comparison of the calculated ternary invariant points,

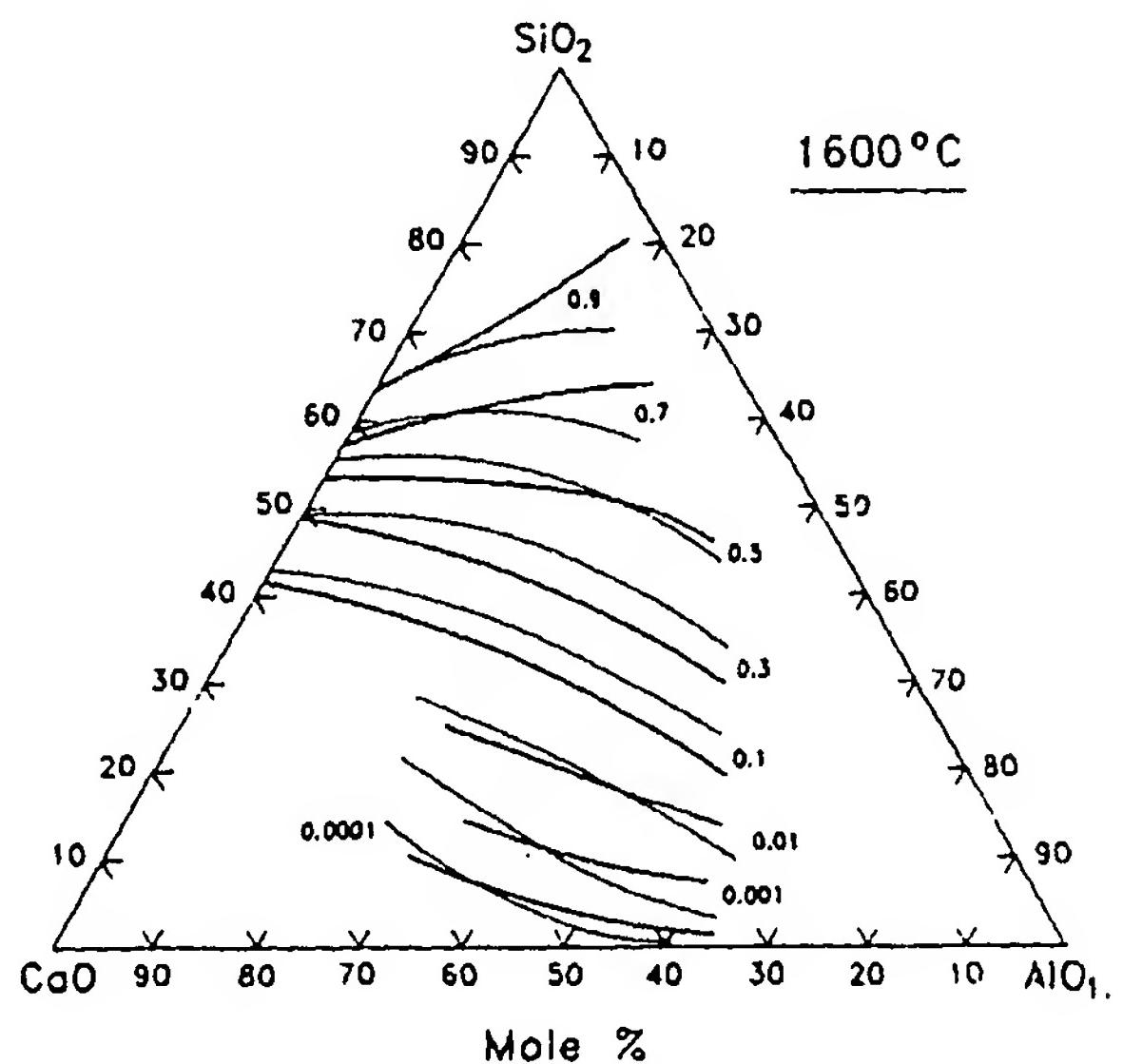


Fig. 6—SiO<sub>2</sub> Activities (solid standard state) in CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> slag at 1600 °C. Compositions in mole pct of components CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>. — Measured<sup>1711,1721</sup> and - - - calculated.

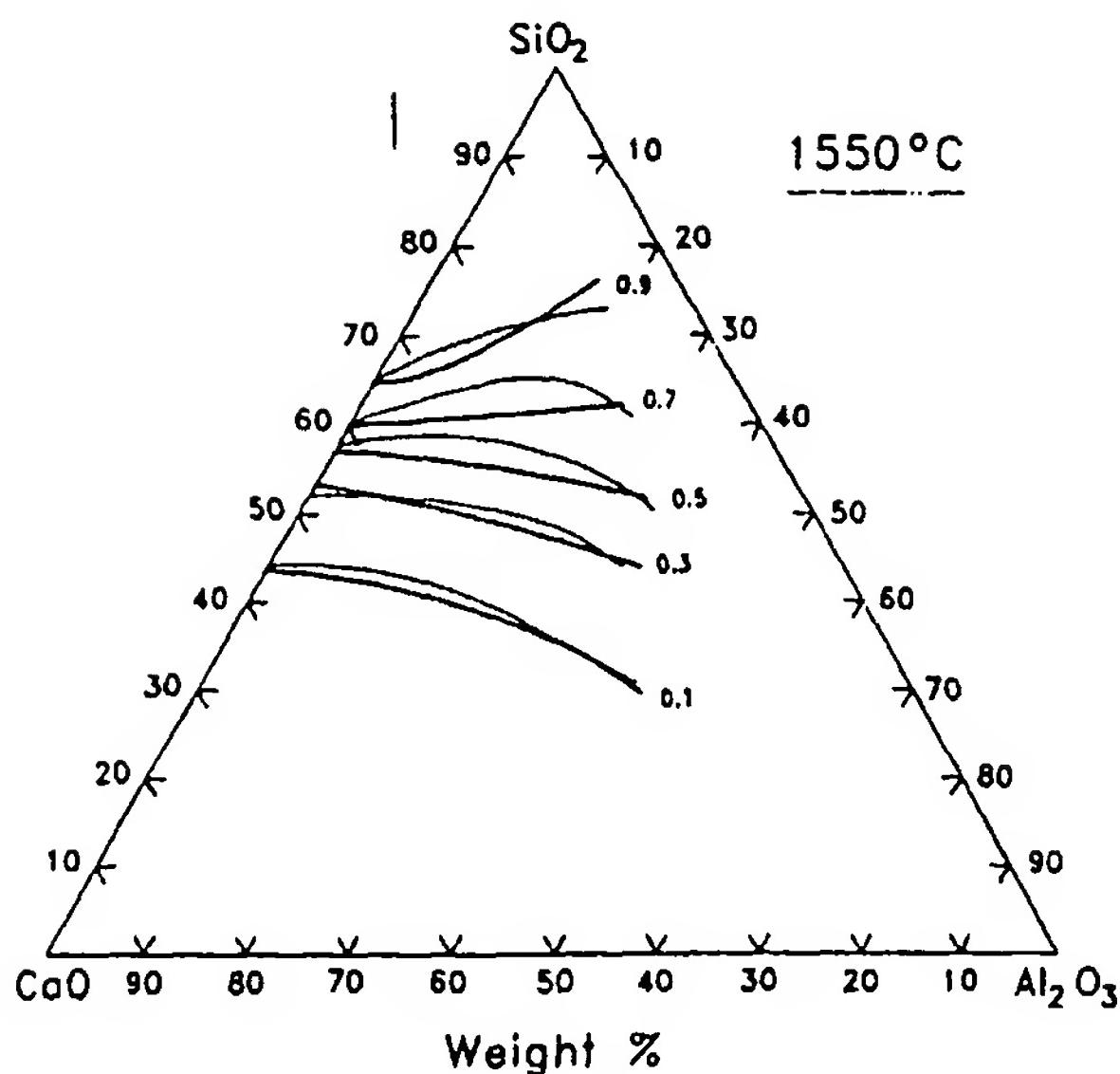


Fig. 7— $\text{SiO}_2$  activities (solid standard state) in  $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  Slags at  $1550^\circ\text{C}$  — measured<sup>14,60</sup> and — Calculated.

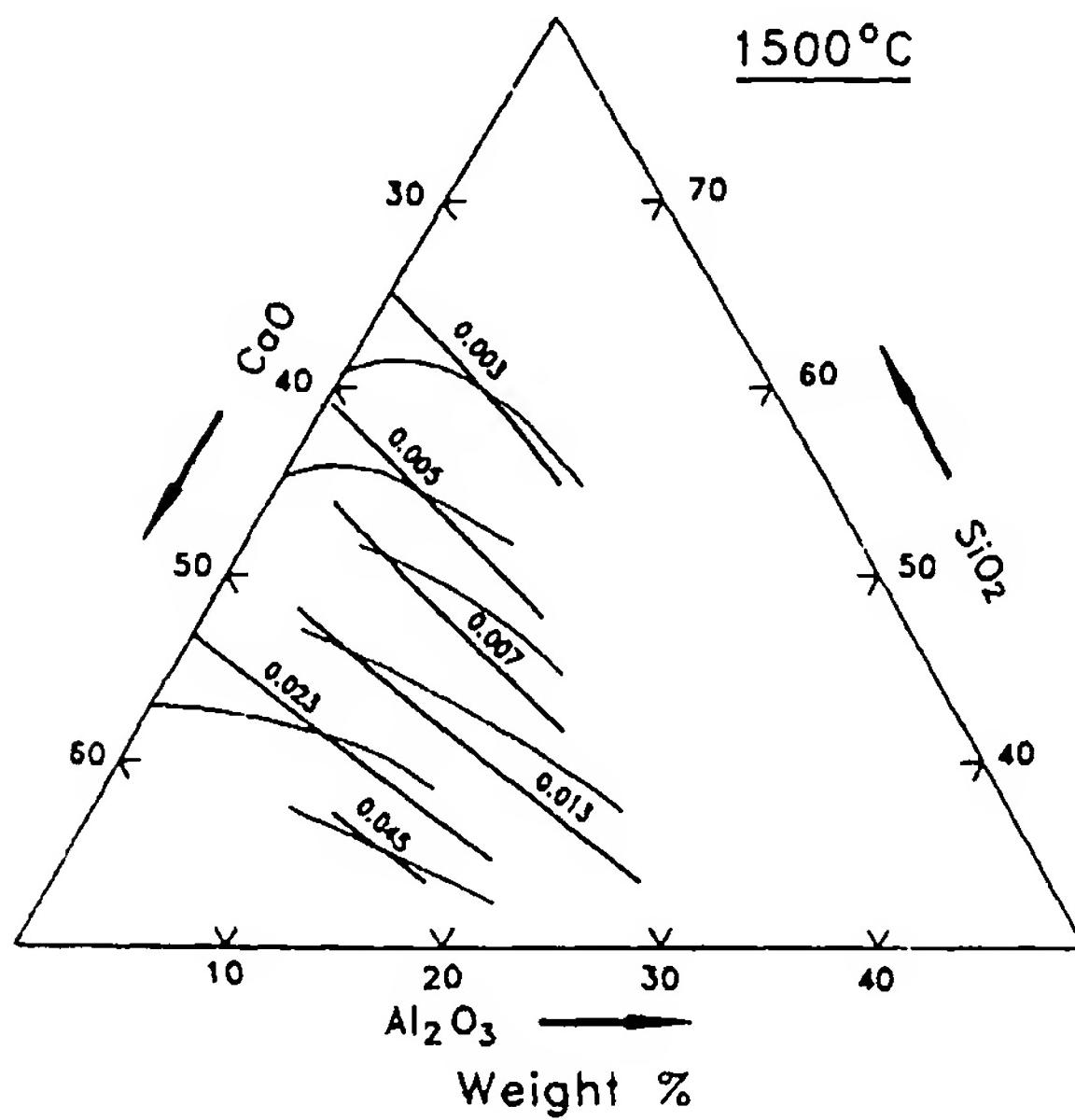


Fig. 8—CaO Activities (solid standard state) in  $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  slags at  $1500^\circ\text{C}$ . — Measured<sup>14,61</sup> and — Calculated.

saddle points, and congruent melting points from the optimized phase diagram with those from the composite diagram of Osborn and Muan<sup>160</sup> is shown in Table II. The largest differences occur in those regions where the experimental measurements are sparse and where there is the greatest disagreement among measurements. At all points, the agreement is within experimental error limits.

Calculated silica activities are compared with the experimental data in Figures 6 and 7. Again, agreement is within experimental error limits, the accord between the experimental and calculated values being generally as good

as that between the two sets of measurements. For  $\text{SiO}_2$  activities below 0.01, the calculated values are higher than the reported values in Figure 6 at higher  $\text{Al}_2\text{O}_3/\text{CaO}$  ratios. It is difficult to see how the  $\text{SiO}_2$  activities could be as low as the reported<sup>168,69,711</sup> values, since extrapolation to the  $\text{SiO}_2-\text{Al}_2\text{O}_3$  binary would then result in very low  $\text{SiO}_2$ -activities in this system, contrary to the binary assessment discussed in Section V.

The activity data of Kalyanram *et al.*<sup>172</sup> in Figure 8 were not included in the least-squares optimization, because their results in the  $\text{CaO}-\text{SiO}_2$  binary system do not agree well with the optimized  $\text{CaO}$ -activities in this binary. However,  $\text{CaO}$ -activities calculated from the optimized parameters agree very well with the data of these authors in the ternary system as can be seen in Figure 8. The probable maximum inaccuracy in the assessed diagram is estimated as  $\pm 35^\circ\text{C}$  or  $\pm 3$  mol pct.

## VIII. CONCLUSIONS

Critical evaluations of all available reliable thermodynamic and phase diagram data for the  $\text{CaO}-\text{Al}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3-\text{SiO}_2$  binary systems have been conducted. Through the technique of least-squares optimization, all data were evaluated simultaneously to obtain one set of self-consistent model coefficients for the Gibbs energies of all phases as functions of temperature and composition. The evaluations are valid from room temperature to above the liquidus temperatures. For all compounds and the liquid solutions, the present evaluations are considered to give the most reliable currently available estimates of the true values of the thermodynamic properties. The phase diagrams, calculated thermodynamically from the same optimized parameters, are considered to be the most reliable currently available estimates of the true phase diagrams. The modified quasichemical model was used to represent the thermodynamic properties of the binary liquid slags with a small number of parameters.

With these binary parameters and those from the optimization of the  $\text{CaO}-\text{SiO}_2$  system reported previously,<sup>111</sup> the quasichemical model was used to predict the thermodynamic properties of the slag phase in the  $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  ternary system. Two additional small ternary parameters were required to reproduce all available ternary phase diagrams and thermodynamic data to within experimental error limits.

The calculated optimized ternary phase diagram is consistent with the ternary activity data, with the Gibbs energies of formation of all compounds, and with the most recent critically assessed phase diagrams of the three binary subsystems. All isotherms and univariant lines have been interpolated according to correct thermodynamic principles. For these reasons, the calculated phase diagram is considered to be the most reliable currently available estimate of the true diagram.

In many ternary systems containing  $\text{SiO}_2$  with two basic oxides, very good predictions of the thermodynamic properties of the slags and of the ternary phase diagrams have been obtained with the quasichemical model by using only parameters from the binary systems.<sup>14,5,7-9,11,121</sup> The present calculations show that even in a system containing the amphoteric oxide  $\text{Al}_2\text{O}_3$ , quantitative results can be obtained with only a very few small ternary parameters.

**EXHIBIT D**

# Struktur und Eigenschaften von Schlacken der Metallhüttenprozesse Dichtebestimmungen und elektrische Leitfähigkeitsmessungen an Schmelzen des Systems Kalk-Tonerde-Kieselsäure<sup>a)</sup>

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Im Temperaturbereich von 1350 bis 1550 °C wurden die Dichte und das elektrische Leitvermögen von 26 Schmelzen des Systems CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> im Konzentrationsgebiet von 35 bis 60% CaO, 5 bis 20% Al<sub>2</sub>O<sub>3</sub> und 30 bis 60% SiO<sub>2</sub> ermittelt. Die Bestimmung der Dichte erfolgte nach dem Archimedischen Prinzip durch Messung des Auftriebs. Die elektrische Leitfähigkeit der Schmelzen wurde mittels einer Thomson-Federsstrombrücke gemessen. Die Versuchsergebnisse wurden in Schaubildern zusammengefaßt und diskutiert.

Dem umfangreichen Schrifttum über die Eigenschaften von Schmelzen des Systems Kalk-Tonerde-Kieselsäure sind bisher nur wenige Untersuchungen über die Dichte und das elektrische Leitvermögen zu entnehmen. Vegen der großen Bedeutung dieser Silikatschmelzen für die praktische Durchführung von Schmelzprozessen in den verschiedenen Zweigen der Hüttenindustrie wurden in Weiterführung der Institutsuntersuchungen über die Konstitution und die Eigenschaften von Schlacken die elektrische Leitfähigkeit und die Dichte einer Reihe synthetischer Schmelzen des Systems CaO - Al<sub>2</sub>O<sub>3</sub> - SiO<sub>2</sub> im Konzentrationsbereich (Gew.-%) 35 bis 50 CaO, 5 bis 20 Al<sub>2</sub>O<sub>3</sub> und 30 bis 60 SiO<sub>2</sub> bestimmt.

## Schrifttumsübersicht

Dichtemessungen im System CaO - Al<sub>2</sub>O<sub>3</sub> - SiO<sub>2</sub> liegen vor von Barret u. Thomas [1]<sup>b)</sup> sowie von Hopel u. Jessin [2]. In beiden Arbeiten wurde die Dichte der Schmelzen nach der Methode des maximalen Blasendrucks bestimmt. Während Barret und Thomas bis zu Temperaturen von 1670 °C die Dichtewerte von 10 synthetischen Silikatschmelzen der Zusammensetzungen (Gew.-%) 15 bis 39 CaO, 10 bis 40 Al<sub>2</sub>O<sub>3</sub> und 30 bis 65 SiO<sub>2</sub> ermittelten, erstreckten sich die Untersuchungen der letztgenannten Autoren auf 5 Schmelzen, die sich in der Zusammensetzung nur wenig unterscheiden und außerdem Eisengehalte von 1 bis 3 % aufweisen. Ein Vergleich mit den eigenen Meßwerten ist wegen des starken Einflusses des Eisens auf die Dichte nicht möglich.

In einer Versuchseinrichtung, die aus einem zwischen zwei Graphitplatten eingespannten Kohletiegel und zwei in das Schlackenbad eintauchenden Graphitelektroden bestand, bestimmten 1924 Farup, Fleischer u. Holtan [3] bis zu Temperaturen von 1500 °C das elektrische Leitvermögen binärer CaO-SiO<sub>2</sub>-Schmelzen mit 30, 35, 45 und 50 Gew.-% CaO und ferner von 14 schmelzflüssigen Silikaten des Systems CaO - Al<sub>2</sub>O<sub>3</sub> - SiO<sub>2</sub> im Konzentrationsbereich von 15 bis 50% CaO, 5 bis 15% Al<sub>2</sub>O<sub>3</sub> und 40 bis 70% SiO<sub>2</sub>.

Im Rahmen von Untersuchungen über die Leitfähigkeits-Temperaturbeziehungen von Hochofenschlacken in schmelzflüssigem Zustand wurde von Markin u. Derge [4] im Temperaturbereich von 1450 bis

1600 °C die elektrische Leitfähigkeit von 15 synthetischen Silikatschmelzen im Konzentrationsbereich von 35 bis 50% CaO, 5 bis 20% Al<sub>2</sub>O<sub>3</sub> und 35 bis 50% SiO<sub>2</sub> ermittelt. Die Untersuchungen wurden in einem geschlossenen Induktionsofen durchgeführt. Die Schlackenschmelzen befanden sich in einem Graphitiegel, in den zwei Graphitelektroden eingeführt wurden. Die Bestimmung des Badwiderstandes erfolgte mit einer Wheatstone-Brücke in Verbindung mit einem akustischen Nullpunktsabgleich.

Über den Einfluß von FeO und SiO<sub>2</sub> auf die elektrische Leitfähigkeit von 3 Ausgangsschlacken des Systems CaO - Al<sub>2</sub>O<sub>3</sub> - SiO<sub>2</sub> geben die Versuchsreihen von Hofmann u. Marincek [5] Aufschluß. Die Schlacken wurden in einem Platintiegel erschmolzen, der gleichzeitig als eine der beiden Meßelektroden diente. Als zweite Elektrode tauchte zentral ein Platin-draht in das Schmelzbad ein. Der elektrische Widerstand des Schmelzbades wurde mittels einer Philips-Meßbrücke (Meßfrequenz 50 Hz) gemessen.

Im Rahmen der Institutsuntersuchungen über die Dichte und elektrische Leitfähigkeit von CaO - Al<sub>2</sub>O<sub>3</sub> - SiO<sub>2</sub>-Schmelzen wurden zwei Meßreihen durchgeführt, wobei in den vorläufigen Versuchen von Greiner [6] insbesondere die meßtechnischen Probleme und die Schwierigkeiten bei der Herstellung blasenfreier, homogener Schlackenschmelzen eingehend behandelt wurden. Über die gesamten bisher durchgeführten Untersuchungen, die sich auch auf das quaternäre System CaO - Al<sub>2</sub>O<sub>3</sub> - MgO - SiO<sub>2</sub> erstrecken, wurde ausführlich berichtet [7].

## Herstellung und Zusammensetzung der untersuchten Schlackenproben

Als Ausgangsmaterialien für die Herstellung der synthetischen CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-Schmelzen dienten folgende Chemikalien der Firma E. Merck, Darmstadt:

SiO<sub>2</sub>: gewaschen und geäugt, p. a.

CaO: p. a.

Al<sub>2</sub>O<sub>3</sub>: wasserfrei, reinst ( $\gamma$ -Tonerde).

Vor der Einwaage wurden die einzelnen Substanzen zunächst auf eine einheitliche Korngröße von 250  $\mu\text{m}$  gebracht. Die Gesamteinwaage einer jeden Schlackenprobe wurde so berechnet, daß sie im Versuchstiegel (Pt/Rh-Tiegel, Volumen ca. 45 cm<sup>3</sup>) eingeschmolzen werden konnte. Um eine möglichst homogene Mischung der einzelnen Komponenten sicherzustellen, wurde jede

<sup>a)</sup> Über die Arbeiten I bis IV dieser Untersuchungsreihe wurde berichtet in Erzmetall 9 (1956), S. 207 - 214; 13 (1960), S. 363 - 373; 14 (1961), S. 319 - 328; 14 (1961), S. 441 - 450.

<sup>b)</sup> Siehe das Schrifttumsverzeichnis am Schluß der Arbeit.

Schlackenprobe nach der Einwaage in einer Kugelmühle mechanisch vermischt und in den Meßtiegel eingefüllt. Nach dem Einschmelzen der Oxidgemische im Vakuum-Induktionsofen wurden die Schmelzen bis zur vollständigen Läuterung und Blasenfreiheit im Vakuum (bis 1 Torr) belassen. Die vollkommen homogenen und klargeschmolzenen Einwaagen wurden dann in den eigentlichen Hochtemperaturmeßofen eingesetzt. Chemisch-analytische Untersuchungen nach den Versuchsreihen ergaben, daß die Zusammensetzungen der Schlacken weniger als  $\pm 0,5\%$  von ihrem Sollwert abweichen.

Über die Zusammensetzung der 26 untersuchten Schlacken geben Zahlentafel 1 und das in Bild 1 wieder.

Zahlentafel 1  
Zusammensetzung der untersuchten Schlacken in Gew.-%

Schl. Nr.	CaO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Schl. Nr.	CaO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>
1	35	5	60	14	45	6	49
2	35	10	55	15	45	8	47
3	35	15	50	16	45	9	46
4	35	18	47	17	45	10	45
5	35	19	46	18	45	15	40
6	35	20	45	19	45	20	35
7	40	5	55	20	50	5	45
8	40	10	50	21	50	10	40
9	40	13	47	22	50	15	35
10	40	14	46	23	50	20	30
11	40	15	45	24	43,6	11,4	45
12	40	20	40	25	42,6	11,4	46
13	45	5	50	26	41,6	11,4	47

gegebene Teildiagramm des Systems CaO – Al<sub>2</sub>O<sub>3</sub> – SiO<sub>2</sub>, Aufschluß. Die in dem Zustandsschaubild eingetragenen Phasengrenzen und Liquiduslinien sind dem Diagramm von Rankin u. Wright [8] sowie Greig [9] entnommen. Aus der Darstellung der Schmelzflächen dieses Teilsystems ist zu ersehen, daß für die vorliegenden Untersuchungen Schlackenzusammensetzungen der Pha-

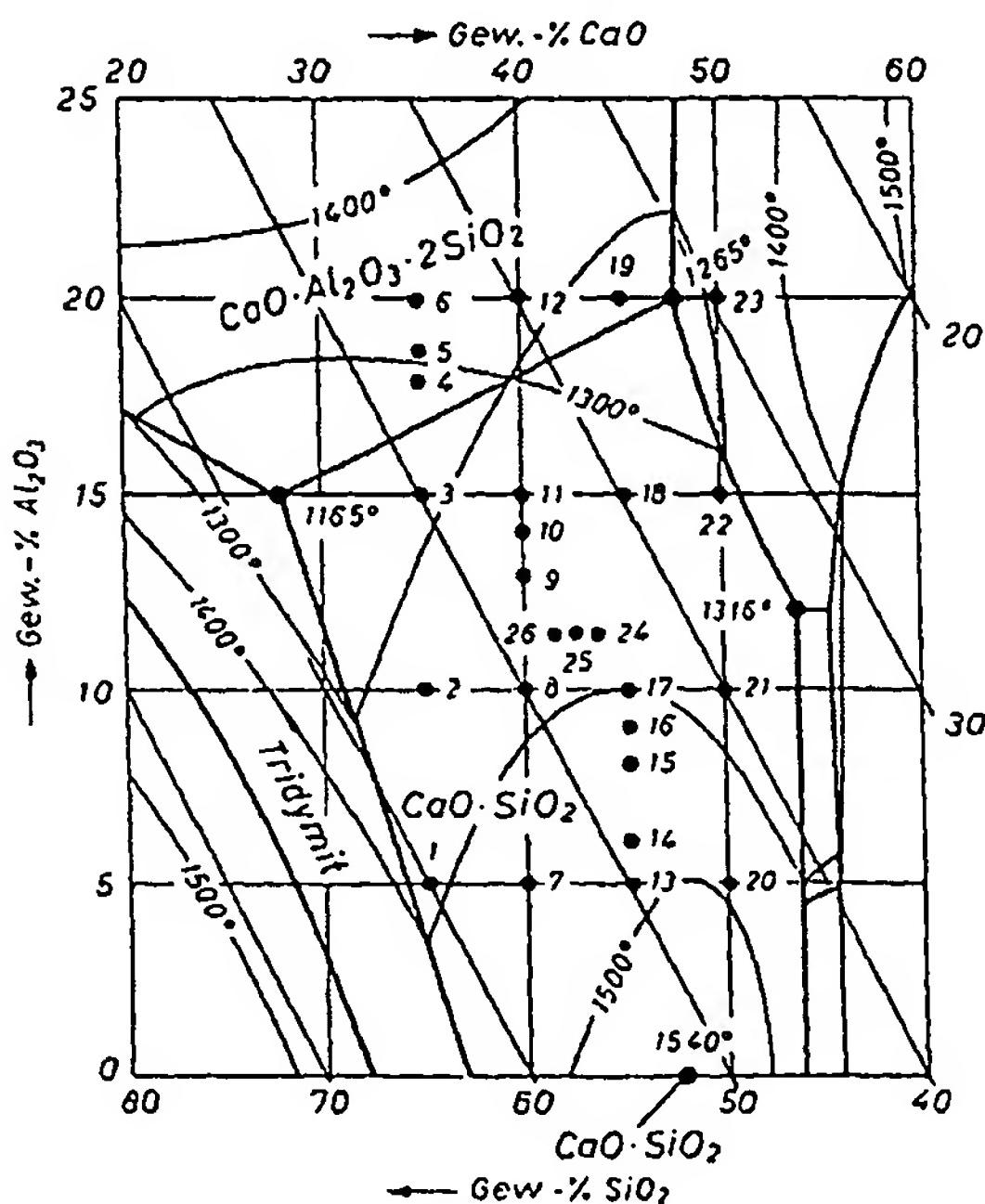


Bild 1. Teildiagramm des Systems CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> mit Angaben über die Lage der untersuchten Schlacken

sengebiete Wollastonit (CaO·SiO<sub>2</sub>) und Anorthit (CaO·Al<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub>) gewählt wurden. Sie zeichnen sich durch sehr niedrige Schmelzpunkte aus, die für die Dreistoff-Eutektika bei 1165, 1265 und 1316 °C liegen. Silikatschmelzgemische dieses Konzentrationsbereiches bilden — wie aus einer Übersicht [10] über die Zusammensetzungen technischer Schlacken hervorgeht — die Hauptkomponenten einer Vielzahl von Betriebschlacken der Eisenhüttenprozesse und anderer schmelzmetallurgischer Metallgewinnungsverfahren.

#### Versuchsaufbau und Versuchsdurchführung

In Bild 2 ist schematisch der Aufbau von Ständer und Führungen für den Hochtemperaturofen und die Meßeinrichtungen wiedergegeben. Als Ständer und Führung für die Halterung (1) des Hochtemperaturofens (2) sowie für die Halterung und Führung (3) der Wägevorrichtung für die Dichtebestimmungen und die Leitfähigkeitsmeßeinrichtung diente ein Vierkant-

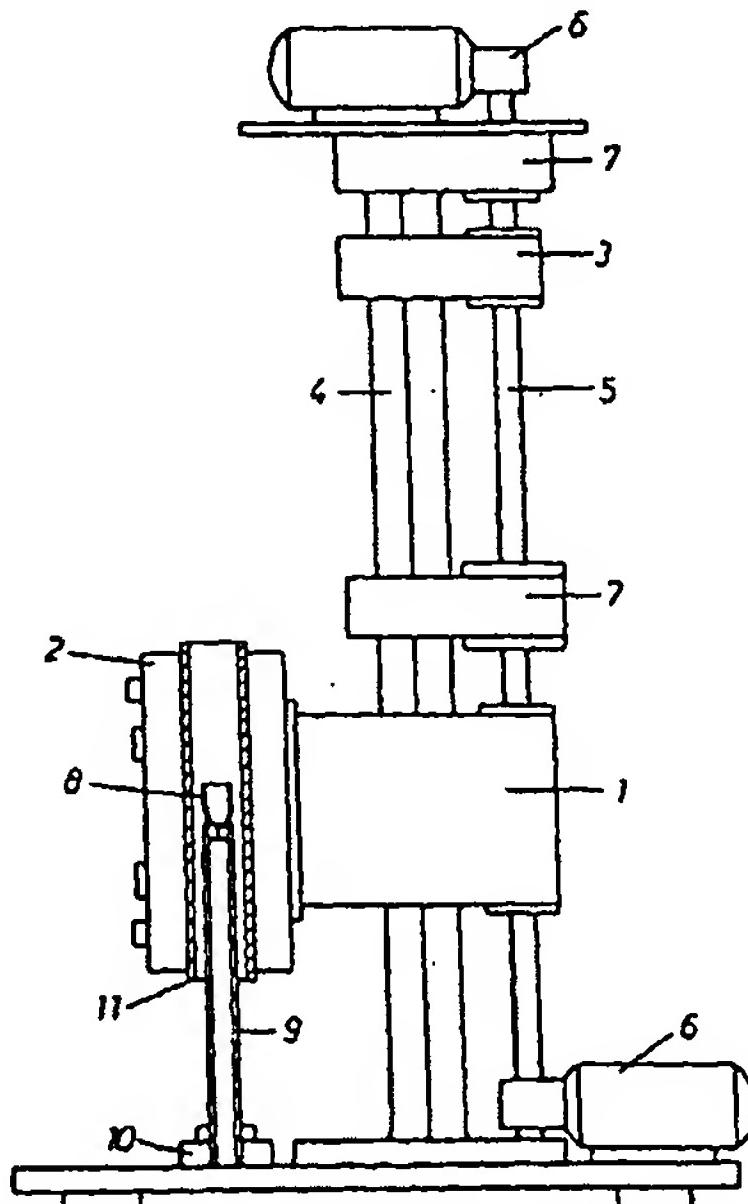


Bild 2. Versuchseinrichtung. Erläuterungen im Text

profil (4). Die Anordnung gestattet ein getrenntes Heben und Senken von Ofen und Meßeinrichtungen. Die Auf- und Abwärtsbewegung erfolgt mittels einer Gewindespindel (5), die durch zwei stufenlos regelbare Getriebemotoren (6) angetrieben wird. Die Spindel hat eine Steigung von 3 mm je Umdrehung. Mittels einer auf dem Tellerrand des mittleren Lagerfußes (7) angebrachten Feinskala ist das Eintauchen der Elektroden bis auf ca.  $1/100$  mm genau zu kontrollieren. Das Heben und Senken von Ofen und Meßeinrichtungen kann entweder unmittelbar an der Versuchseinrichtung oder durch Fernbedienung aus dem Meßraum gesteuert werden. Der in der temperaturkonstanten Zone des Ofens befindliche Pt/Rh-Meßtiegel (8) steht auf einem Sintertonederohr (9), welches durch einen Spannkopf (10) gehalten wird. Der Spannkopf ist auf der Grundplatte des Ständers verschraubt. Die Beheizung des Ofens erfolgt mittels einer Rhodiumband-Wicklung auf der Außenseite des Sintertonederohres (11). Das Heizrohr ist an seinen Stirnseiten mittels keramischer

Formringe in einem äußeren Ofenkörper aus Stahlblech gelagert. Die Ofentemperatur wurde über ein in einer Längsnut des Heizrohres untergebrachtes Thermoelement in Verbindung mit einem Fallbügelregler (Meßbereich 3 mV) geregelt. Höhere Thermospannungen wurden durch Gegenschaltung einer in 3-mV-Stufen einstellbaren konstanten Spannungsquelle kompensiert. Um die Temperaturschwankungen möglichst klein zu halten, wurde ein Teil der Heizspannung, die zweistufig einstellbar ist, zu- bzw. gegengeschaltet. Die Temperatur der Schmelzen wurde mit einem Pt-Pt/Rh-Thermoelement gemessen. Bei den Leitfähigkeitsmessungen war die Lötstelle des Thermoelements oberhalb der Meßelektroden angeschweißt. Bei den Dichtebestimmungen befand sich die Lötstelle direkt an der Außenwand des Meßtiegels. Als Kaltlötstelle diente ein konstant auf 50 °C gehaltenes Wasserbad. Als Anzeigegerät wurde wahlweise ein Präzisions-Millivoltmeter oder ein Thermoschreiber verwendet. Überprüfungen des Regelkreises bei 1500 °C ergaben auf dem Thermoschreiber für Abweichungen  $\pm 2$  °C noch deutlich sichtbaren Ausschlag gegenüber einer Geraden bei Temperaturkonstanz.

### Dichtemessungen

Die Bestimmung der Dichte erfolgte nach dem Archimedischen Prinzip durch Messung des Auftriebs, den ein Senkkörper bekannten spezifischen Gewichts beim Eintauchen in die zu untersuchende Schmelze erfährt. Diese Meßmethode ist — wie Bockris, Tomlinson u. White [11] im Rahmen von Dichtebestimmungen schmelzflüssiger Li<sub>2</sub>O-, K<sub>2</sub>O- und Na<sub>2</sub>O-Silikate aufzeigen konnten — auch für Silikatschmelzen anwendbar. Ungenaue Gleichgewichtscinstellungen der Waage bei zähflüssigeren Schmelzzusammensetzungen (>50 P) lassen sich dadurch umgehen, daß man durch Änderung der Auflagegewichte die Auf- und Abwärtsbewegung des Senkkörpers ermittelt und die Meßwerte auf die Geschwindigkeit 0 extrapoliert. Der Einfluß der Oberflächenspannung läßt sich bei dieser Methode durch Messungen mit zwei verschiedenen Senkkörpern an Drähten gleichen Durchmessers eliminieren.

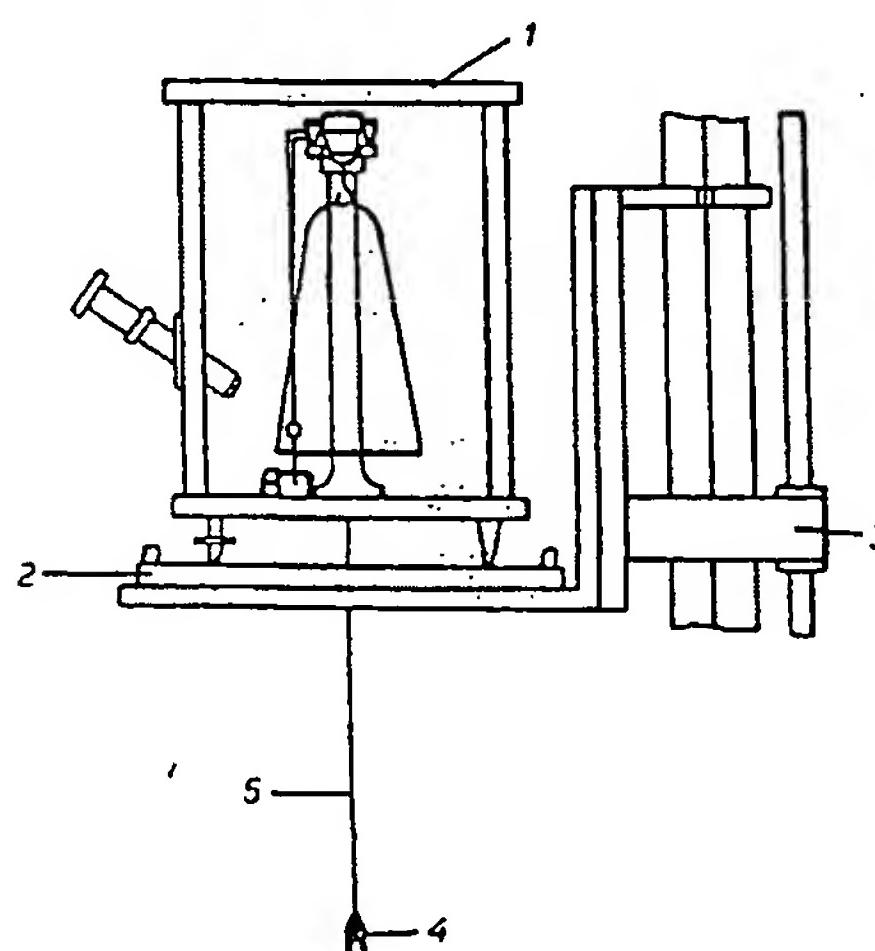


Bild 3. Dichte-Meßeinrichtung. Erläuterungen im Text

Die bei den Dichtebestimmungen verwendete Versuchseinrichtung ist in Bild 3 dargestellt. Zur Ermittlung des Auftriebs diente eine für diesen Zweck um-

gebauete Analysenwaage (1), die auf einer wassergekühlten Unterlage (2) an der Halterung (3) (vgl. Bild 2) über dem Hochtemperaturofen angebracht war. Den in die Schmelze eintauchenden Senkkörper bildete ein an beiden Enden spitz zulaufender, massiver Pt/Rh-Zylinder (4). Der Senkkörper wurde an einen dünnen Pt/Rh-Aufhängedraht (5) angeschweißt. Der Draht war an einem der Waagebalken befestigt und wurde durch kleine Bohrungen am Boden der Waage und im Ofenschluß in das Innere des Ofens geführt.

Um eine möglichst genaue Geschwindigkeitsbestimmung der Auf- und Abwärtsbewegung des Senkkörpers sicherzustellen, wurde die Zeit, die der Meßkörper zum Durchlaufen einer vorgegebenen Weglänge benötigt, elektrisch gestoppt. Hierbei läßt sich die durch den Zeigeranschlag der Waage vorgegebene Weglänge des Senkkörpers mit Hilfe zweier Kontaktstifte einstellen. Die Arretierungsvorrichtung der Waage ist gleichzeitig so konstruiert, daß bei der Loslösung des Zeigers ein elektrischer Stromkreis geschlossen und dadurch eine Relais-Stoppuhr betätigt wird. Berührt der von dem einen Kontakt gelöste Zeiger den anderen Kontaktstift, wird ein Stromkreis geschlossen, der die Uhr stoppt.

Die Dichte  $d$  der Silikatschmelzen errechnet sich aus den Meßwerten anhand der Beziehung

$$d = \frac{A}{V_t} = \frac{G_L - G_S}{V_t} [\text{g/cm}^3].$$

Es bedeuten:  $A$  = Auftrieb des Senkkörpers,  $V_t$  = Volumen des Senkkörpers bei der Versuchstemperatur  $t$ ;  $G_L$  und  $G_S$  = Gewichte des Senkkörpers in Luft bzw. Schlackenschmelze.

Die Eichung des Senkkörpers erfolgte bei Raumtemperatur in destilliertem Wasser. Die Umrechnung des Eintauchkörper-Volumens von Raum- auf Versuchstemperatur geschah mit Hilfe des aus dem Schrifttum [12] bekannten Ausdehnungskoeffizienten für Pt/Rh 80/20. Um beim Einbringen des Pt/Rh-Zylinders in die Schmelze die Eintauchtiefe genau einzustellen zu können, wurden Senkkörper und Meßtiegel mit einer Stromquelle verbunden und die Badberührung des Senkkörpers an einem Amperemeter abgelesen. Die Dichtemessungen wurden alle bei gleicher Eintauchtiefe des Senkkörpers durchgeführt.

### Leitfähigkeits-Bestimmungen

Als Leitfähigkeitsmeßbrücke diente eine Thomson-Wechselstrombrücke, die ursprünglich von Winterhager u. Werner [13] für Bestimmungen des elekt-

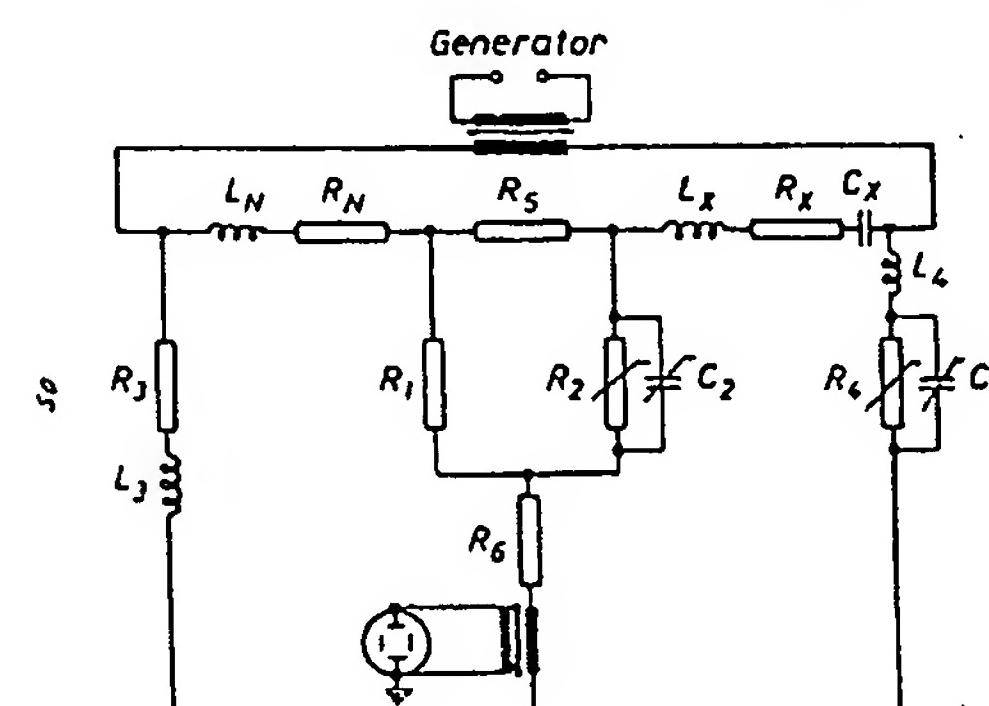


Bild 4. Schaltungsprinzip der Leitfähigkeits-Meßbrücke. Nach Winterhager u. Hoffmann [14]

trischen Leitvermögens von Salzschnellen entwickelt und in ihrem gegenwärtigen Aufbau von Winterhager u. Hoffmann [14] durch eine zusätzliche Impedanz-Analyse für Messungen an Silikatschmelzen bis zu einer maximalen Temperatur von  $1600^{\circ}\text{C}$  ausgelegt wurde. Im Rahmen dieser Arbeiten werden die meßtechnischen Schwierigkeiten und Probleme eingehend behandelt und gelöst. Das Schaltschema der Brücke ist in Bild 4, die Anordnung der Elektroden in Bild 5 dargestellt. Um den Einfluß von Streufeldern zu begrenzen und eine große Stabilität sicherzustellen, erwies sich — wie aus Bild 5 zu ersehen ist — eine ringartige

über Pt/Rh-Drähte (4). Die Badtemperatur wurde mit einem an der Befestigung der Außenelektrode angeschweißten Pt/Pt/Rh-Thermoelement gemessen. Als Halterung und Führung für die Zuleitungen diente ein Tonerderohr (6), das in einer Hülse (7) an einem Kreuzkopf (8, 9, 10) befestigt war. Elektroden und Halterung waren durch ein Sintertonederohr isoliert.

Die Bestimmung der Zellkonstanten erfolgte mit 30 Gew.-%iger Schwefelsäure und mit geschmolzenem Kaliumnitrat bei verschiedenen Temperaturen. Die Leitfähigkeitswerte dieser Eichsubstanzen wurden dem Schrifttum [15] entnommen. Die Zellkonstante beträgt  $0,1737 \text{ cm}^{-1}$ .

Bei der Durchführung der Messungen wurden zunächst vor dem Aufheizen des Ofens die Elektroden mittels des Kreuzgelenkes über der Mitte des Tiegels zentriert. Nach Erreichen einer Temperatur von  $1550^{\circ}\text{C}$  wurden dann die Elektroden auf die Schmelze heruntergefahren und nach Badberührung — zu erkennen am Zusammenfall des Oszillographenbandes — auf eine für alle Schmelzen konstant gehaltene Eintauchtiefe eingestellt und der Ofen mit Asbestschnur abgedichtet. Gemessen wurde im Temperaturbereich von 1350 bis  $1550^{\circ}\text{C}$  bei verschiedenen Frequenzen. Anhand der Meßwerte konnte eine Frequenzunabhängigkeit ab 20 kHz festgestellt werden. Die in dieser Arbeit wiedergegebenen Leitfähigkeitswerte sind aus den bei 50 kHz gemessenen  $R_4$ - und  $C_4$ -Werten anhand der nachfolgenden, von Winterhager u. Hoffmann [14] abgeleiteten und ausführlich behandelten Berechnungs-gleichung ermittelt worden:

$$R_x = [R_3 R_4 (R_N + \omega^2 L_N R_4 C_4) + \\ + (R_N \omega^2 L_3 L_4 - R_3 \omega^2 L_4 L_N) \cdot (1 + R_4^2 \omega^2 C_4^2) + \\ + R_4 \omega L_3 (\omega L_N - R_N R_4 \omega C_4)] : \\ : [(\omega L_3 + R_3 R_4 \omega C_4)^2 + (R_3 - R_4 \omega^2 L_3 C_4)^2]$$

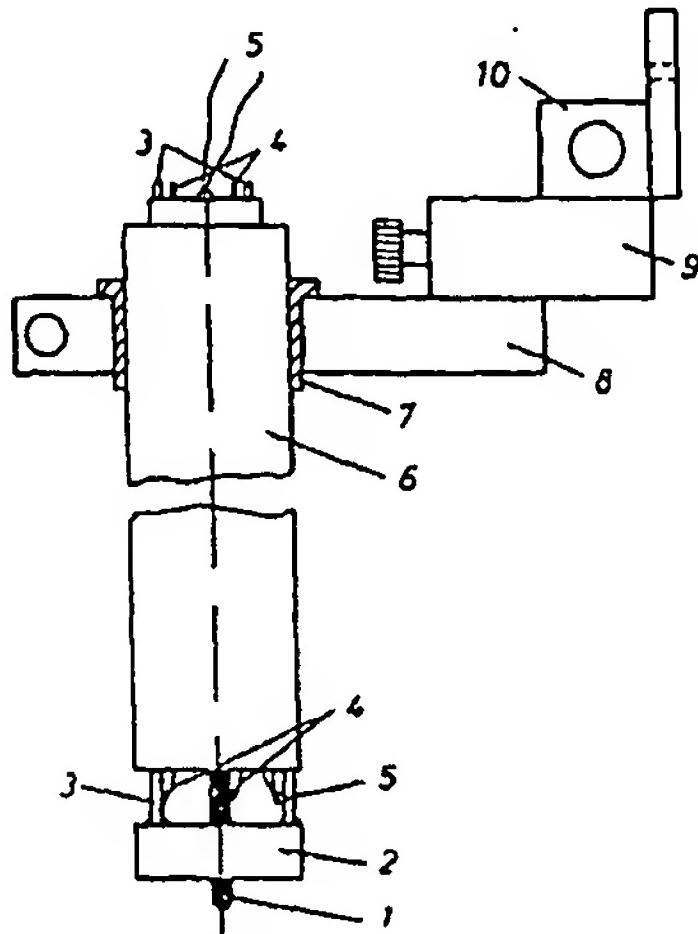


Bild 5. Anordnung der Elektroden. Erläuterungen im Text

Elektrodenform [Pt/Rh-Innenelektrode (1), Pt/Rh-Außenringelektrode (2)] als zweckmäßig. Zur Befestigung der Außenelektrode und als Stromzuführung dienten Pt/Rh-Drähte (3). Der Spannungsabgriff erfolgte

Zahlentafel 2  
Dichte, Molvolumen und Ausdehnungskoeffizient der  $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ -Schmelzen

Schl. Nr. % $\text{Al}_2\text{O}_3$	1350°	Dichte in $\text{g}/\text{cm}^3$			1550 °C	Molvolumen in $\text{cm}^3/\text{mol}$		Ausdehnungskoeffizient $a/\text{°C} \cdot 10^{-5}$
		1400°	1450°	1500°		1350°	1550 °C	
1 60/5	2,531	2,526	2,520	2,513	2,507	23,627	23,854	4,80
2 56/10	2,545	2,537	2,530	2,524	2,517	23,989	24,656	5,65
3 50/16	2,554	2,546	2,539	2,532	2,525	24,414	24,695	5,94
4 47/18	2,559	2,550	2,545	2,540	2,533	24,684	24,937	5,12
5 46/19	2,562	2,553	2,547	2,542	2,534	24,761	25,035	5,53
6	2,563	2,555	2,549	2,543	2,537	24,859	25,113	5,11
7	2,566	2,559	2,550	2,543	2,535	23,223	23,507	6,11
8	2,573	2,565	2,559	2,552	2,543	23,641	23,920	5,90
9	2,586	2,577	2,570	2,562	2,555	23,821	24,110	5,06
10	2,588	2,581	2,573	2,565	2,558	23,903	24,183	5,86
11	2,591	2,584	2,576	2,567	2,561	23,918	24,258	5,84
12	2,604	2,596	2,589	2,581	2,574	24,374	24,658	5,82
13	2,609	2,601	2,594	2,587	2,580	22,760	23,016	5,62
14	2,610	2,603	2,595	2,588	2,580	22,864	23,112	5,82
15	2,613	2,605	2,599	2,591	2,584	23,008	23,266	5,61
16	2,614	2,606	2,601	2,593	2,585	23,092	23,351	5,61
17	2,615	2,609	2,602	2,594	2,587	23,180	23,431	5,41
18	2,624	2,616	2,608	2,601	2,594	23,589	23,862	5,78
19	2,628	2,620	2,614	2,607	2,600	24,063	24,322	5,38
20	2,647	2,640	2,632	2,624	2,617	22,356	22,612	5,72
21	2,657	2,650	2,643	2,635	2,627	22,732	22,992	5,72
22	—	—	2,656	2,648	2,640	—	23,362	6,02
23	—	—	—	2,661	2,653	—	23,748	6,08
24	2,609	2,602	2,595	2,588	2,582	23,394	23,638	5,21
25	2,605	2,597	2,590	2,581	2,578	23,445	23,691	5,25
26	2,600	2,593	2,586	2,580	2,574	23,507	23,745	5,06

Für größere Werte von  $R_x$  als  $0,3 \Omega$  kann man  $L_3$  und  $L_4 = 0$  setzen. Die Gleichung vereinfacht sich dann zu

$$R_x = \frac{R_4(R_3 + \omega^2 L_3 R_4 C_4)}{R_3(1 + R_4^2 \omega^2 C_4^2)}$$

wobei  $R_3 = 1007,6 \Omega$ ,  $R_4 = 10,587 \Omega$  und  $L_3 = 30 \cdot 16 \cdot 10^{-6} \text{ H}$  Konstanten sind. Die Kreisfrequenz  $\omega = 2\pi \cdot r$  beträgt  $314 \cdot 10^3$  bei einem  $r$ -Wert von 50 kHz.

### Versuchsergebnisse

#### Dichtemessungen

Die im Temperaturbereich von 1350 bis 1550 °C ermittelten Dichtewerte  $d$  der CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-Schmelzen sind in Zahlentafel 2 zusammen mit den für 1350 und 1550 °C berechneten Molvolumen (cm<sup>3</sup>/mol) aufgeführt.

Die graphische Wiedergabe der Meßwerte in Bild 6 zeigt, daß im untersuchten Konzentrationsbereich die

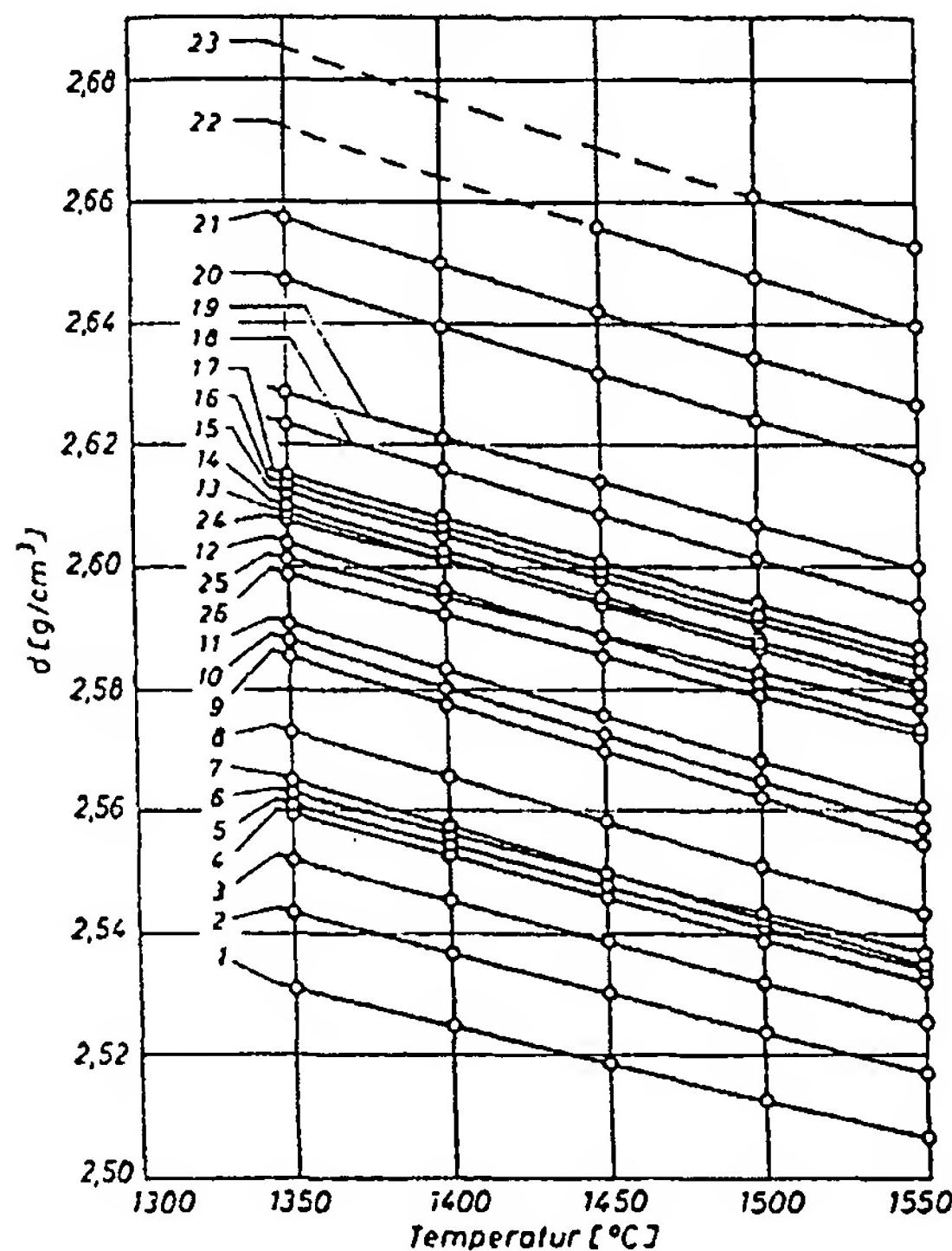


Bild 6. Dichte der CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-Schmelzen in Abhängigkeit von der Temperatur

Dichte der Schlacken stetig mit steigender Temperatur abnimmt. Die sich aus den linearen Dichte-Temperatur-Beziehungen ergebenden Dichte-Temperatur-Koeffizienten  $\alpha$  der Schmelzen sind in Zahlentafel 2 eingetragen. Nach den Gleichungen

$$V_t = V_{1350} [1 + \alpha(t - 1350)]$$

und

$$d_t = \frac{d_{1350}}{1 + \alpha(t - 1350)}$$

können mittels der  $d/t$ -Koeffizienten Molvolumen und Dichte der Schlacken für jede beliebige Temperatur ( $t$  °C) berechnet werden.

Über die Abhängigkeit der Dichte von der Schlackenzusammensetzung gibt Bild 7 Aufschluß. Aus der Wie-

dergabe der Dichtewerte von Schmelzen mit konstanten CaO- und SiO<sub>2</sub>-Gehalten in Abhängigkeit von der Tonerde-Konzentration wird ersichtlich, daß sowohl das Dichte-Temperatur-Verhalten wie auch die Dichte-Zu-

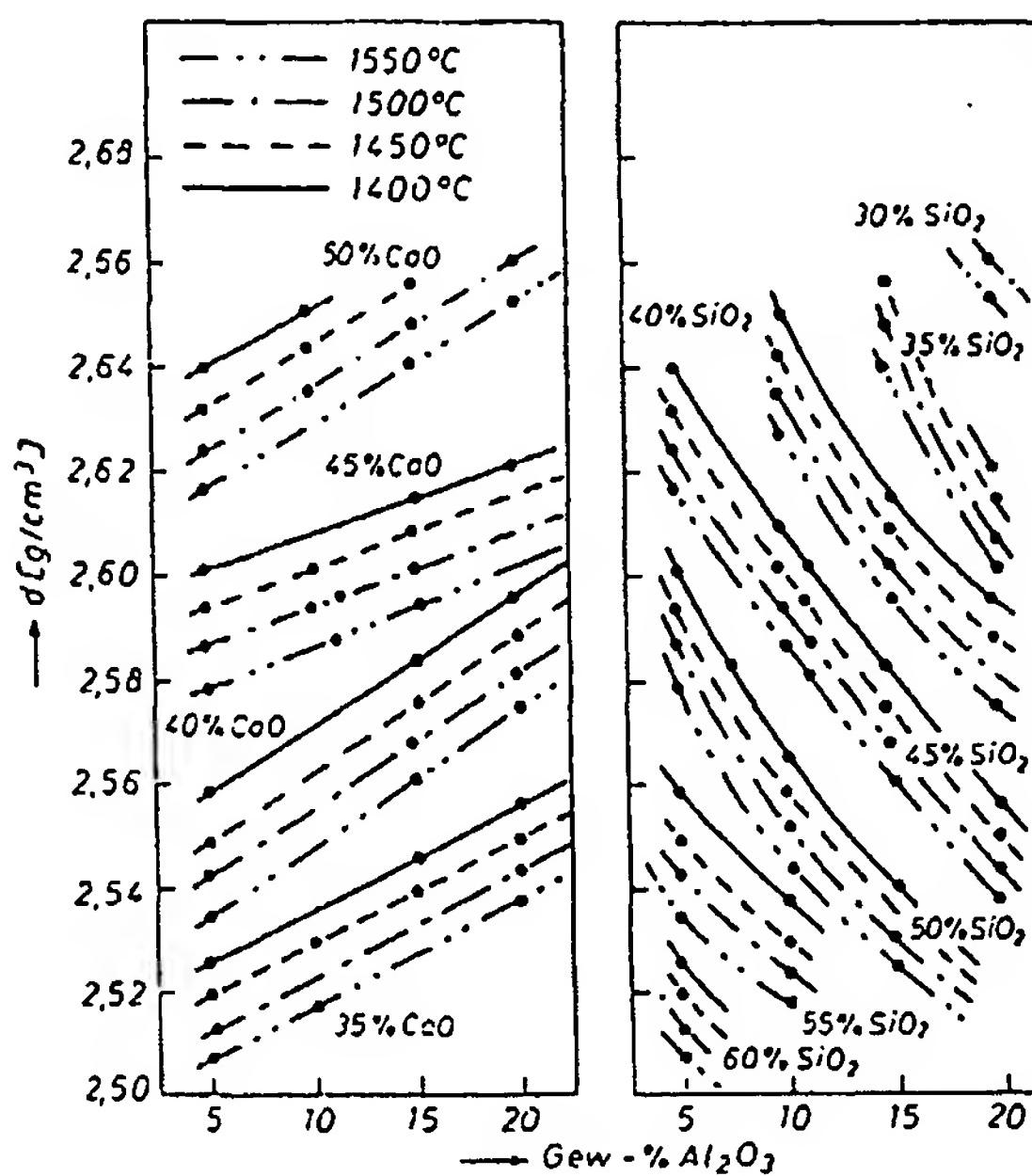


Bild 7. Dichte von Schlacken mit konstantem CaO- und SiO<sub>2</sub>-Gehalt in Abhängigkeit von der Al<sub>2</sub>O<sub>3</sub>-Konzentration

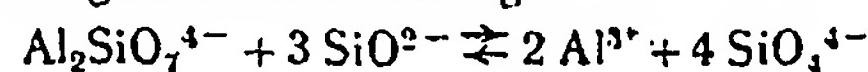
sammensetzungs-Beziehungen dieser Silikatschmelzen über den gesamten untersuchten Temperatur- und Konzentrationsbereich stetig verlaufen. Den Versuchsergebnissen ist zu entnehmen, daß die Dichte der Schlacken mit steigenden Kieselsäurekonzentrationen abnimmt, während bei Zusätzen von CaO eine stärkere Dichte-Zunahme zu verzeichnen ist als bei gewichtsgleichen Zugaben von Al<sub>2</sub>O<sub>3</sub>. Die spezifischen Gewichte (g/cm<sup>3</sup>) der reinen Komponenten im festen Zustand variieren nach Angaben des Schrifttums [15 bis 18] von 3,3 bis 3,4 für CaO, von 2,2 bis 2,6 für SiO<sub>2</sub> und von 2,8 bis 3,82 für Al<sub>2</sub>O<sub>3</sub>.

Für den untersuchten Konzentrationsbereich wurden in der ternären Darstellung in Bild 8 die aus dem Schrifttum [1, 6] bekannten und in dieser Meßreihe ermittelten Versuchsergebnisse für eine Temperatur von 1550 °C zusammengestellt. Aus dem annähernd wiedergegebenen Verlauf der Linien gleicher Dichte ist zu erkennen, daß die Dichte der Schmelzen stetig mit steigenden CaO- und Al<sub>2</sub>O<sub>3</sub>-Gehalten zunimmt. Die Meßwerte von Barret und Thomas [1] sowie Greiner [6] sind im Rahmen der Fehlergenauigkeit in guter Übereinstimmung mit den Ergebnissen der vorliegenden Dichtebestimmungen.

Eine gewisse Gesetzmäßigkeit der Dichte-Konzentrations-Beziehungen kommt in der Auflösung der Dichtewerte in Abhängigkeit vom Verhältnis SiO<sub>2</sub>/CaO (mol.-%), dem sog. Aciditätsgrad der Schmelzen, zum Ausdruck (Bild 9). Der geringe Streubereich der Meßwerte erlaubt eine Kurve auszutragen, die zeigt, daß mit größer werdender Verhältniszahl im Bereich von 0,8 bis 2,0 die Dichte der Schmelzen nahezu linear abnimmt. Diese Ergebnisse deuten darauf hin, daß die Dichte der Kalk-Tonerde-Kieselsäure-Schlacken im

schmelzflüssigen Zustand maßgeblich vom  $\text{SiO}_2/\text{CaO}$ -Verhältnis abhängt. Eine Beeinflussung der Schlackendichte durch die  $\text{Al}_2\text{O}_3$ -Gehalte ist laut Kurvenverlauf erst bei Werten  $< 0,8$  zu verzeichnen. Eine struk-

5 % Maxima, was bei einer konstanten Basizität ( $\text{CaO}/\text{SiO}_2$ ) einem Aktivitätsminimum von  $\text{SiO}_2$  entspricht. Mit zunehmenden  $\text{Al}_2\text{O}_3$ -Gehalten bis 12 % steigt die  $\text{SiO}_2$ -Aktivität bis zu einem Maximum an, um dann linear abzunehmen. Die Verfasser deuten dieses Verhalten gemäß der Gleichung



als eine Umformung von Silikat- und Alumo-Silikat-Anionenkomplexen.

#### Leitfähigkeitsmessungen

Eine Übersicht über die im Temperaturbereich von 1350 bis 1550 °C ermittelten Versuchsergebnisse der

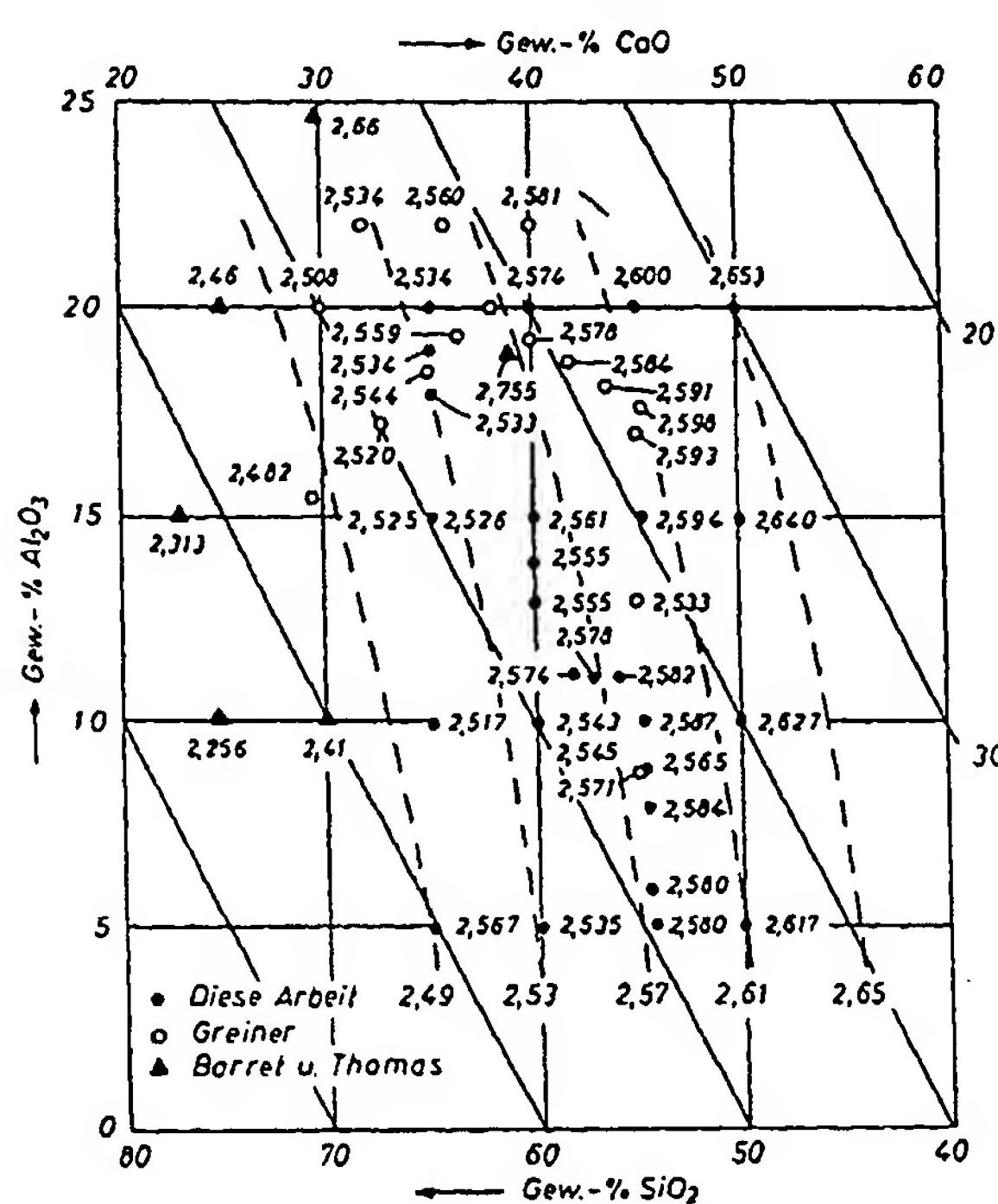


Bild 8. Linien gleicher Dichte bei 1550 °C im Teildiagramm des Systems  $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$

turelle Deutung dieser Erscheinung ist aufgrund der sehr komplexen und noch wenig erforschten Schmelzstruktur der Silikate noch nicht möglich. Es muß daher dahingestellt bleiben, ob diese Dichteabhängigkeit dem

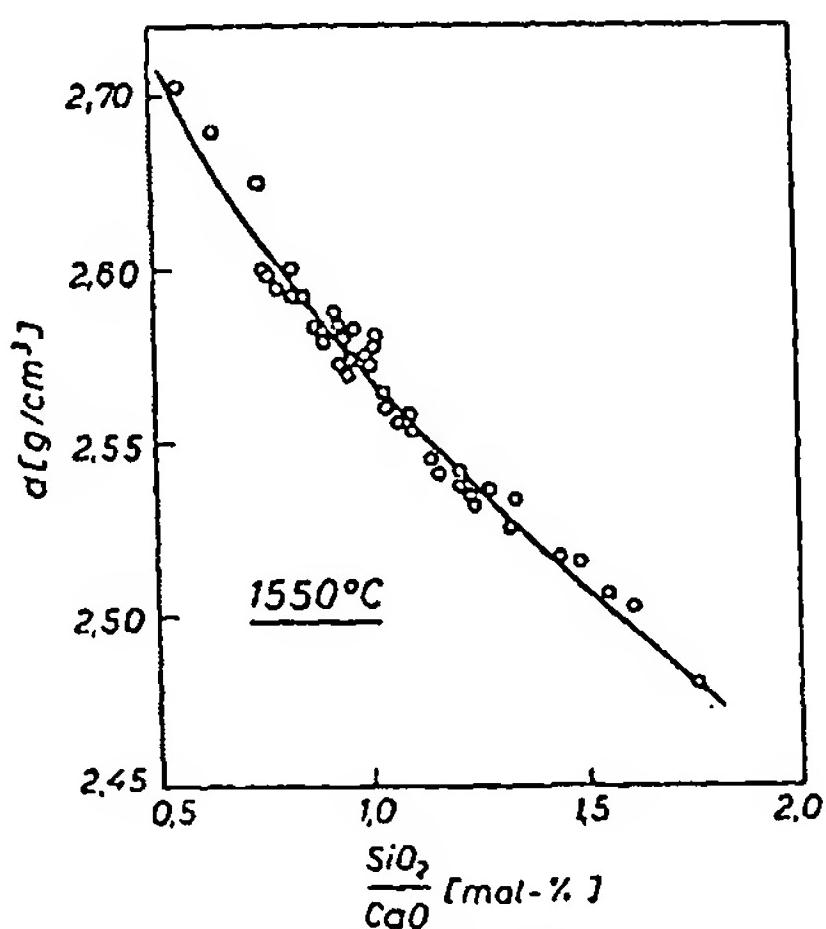


Bild 9. Dichte der  $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ -Schmelzen in Abhängigkeit vom Verhältnis  $\text{SiO}_2/\text{CaO}$

amphoteren Verhalten des Aluminiums oder der Umformung der Schmelzstruktur zuzuschreiben ist. Ein ähnlicher struktureller Einfluß ist beispielsweise den EMK-Messungen von Sanbongi u. Ohmori [19] zu entnehmen. So zeigen die ermittelten Isoaktivitätslinien für  $\text{SiO}_2$  bei  $\text{Al}_2\text{O}_3$ -Konzentrationen um

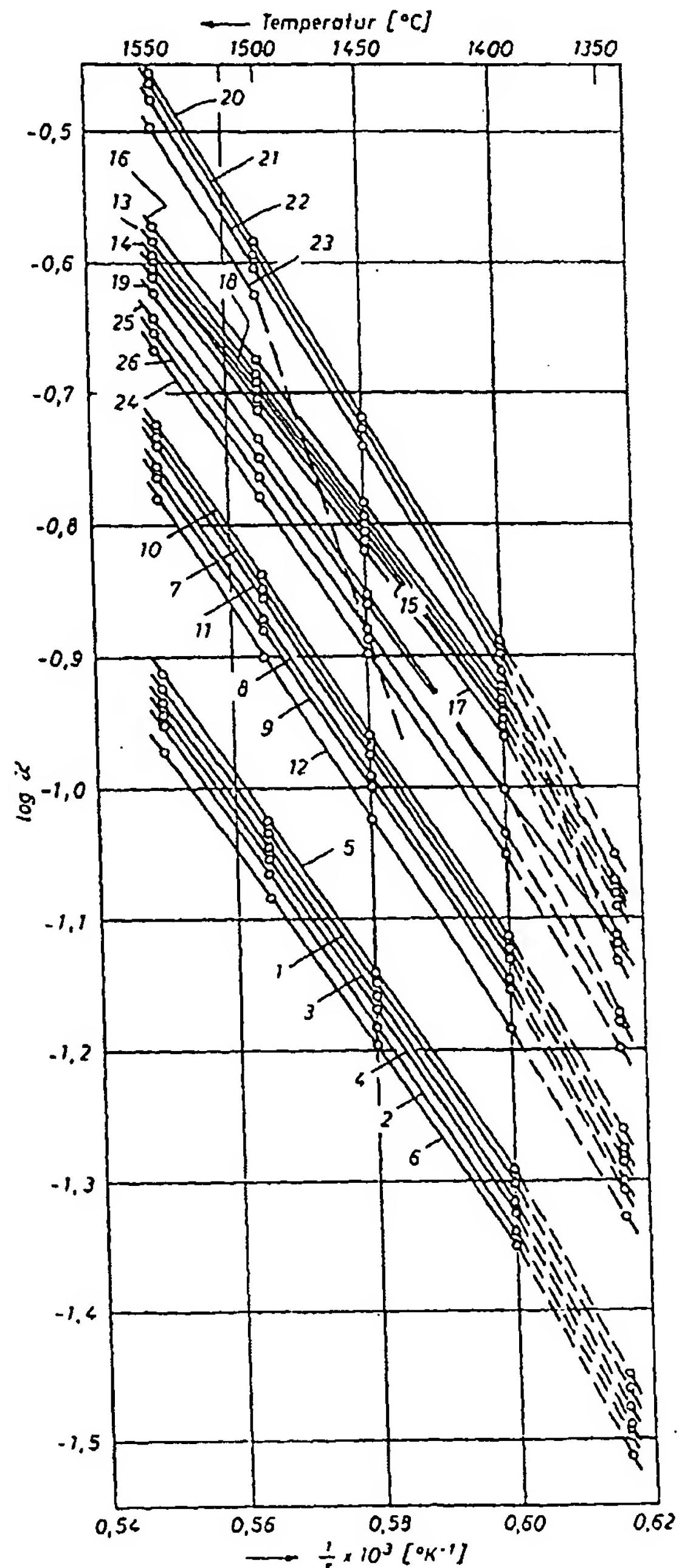


Bild 10. Elektrische Leitfähigkeit der Schlacken in Abhängigkeit von der Temperatur

Zahlentafel 3  
Elektrische Leitfähigkeit der CaO-Al<sub>2</sub>O<sub>3</sub>-Schmelzen

Schl. Nr.	Elektrische Leitfähigkeit $\alpha$ $\Omega^{-1} \cdot \text{cm}^{-1}$					Temperatur-Abhängigkeit von $\log \alpha$	Aktivierungs- Energie $\Delta E$ kcal/mol	Molare Leitfähigkeit bei 1550 °C $A_m$ $\text{cm}^2/\Omega \cdot \text{mol}$
	1350°	1400°	1450°	1500°	1550°C			
1	0,035	0,051	0,071	0,095	0,119	$-8182/T + 3,649$	38,15	2,838
2	0,032	0,047	0,066	0,090	0,116	$-8545/T + 3,774$	39,28	2,813
3	0,034	0,049	0,070	0,094	0,118	$-8576/T + 3,809$	39,51	2,914
4	0,033	0,048	0,069	0,093	0,117	$-8697/T + 3,873$	40,07	2,917
5	0,036	0,052	0,072	0,097	0,123	$-8212/T + 3,619$	37,77	3,079
6	0,031	0,046	0,064	0,085	0,107	$-8061/T + 3,538$	37,61	2,687
7	0,053	0,076	0,106	0,145	0,186	$-8485/T + 3,946$	39,01	4,372
8	0,049	0,072	0,101	0,137	0,176	$-8485/T + 3,922$	39,01	4,210
9	0,048	0,071	0,099	0,135	0,174	$-8458/T + 3,900$	38,86	4,195
10	0,055	0,078	0,109	0,146	0,187	$-8273/T + 3,831$	38,02	4,522
11	0,052	0,075	0,105	0,144	0,185	$-8576/T + 3,994$	39,42	4,487
12	0,047	0,066	0,089	0,129	0,169	$-8848/T + 4,101$	41,62	4,167
13	0,082	0,166	0,159	0,207	0,260	$-7636/T + 3,622$	35,09	5,984
14	0,081	0,114	0,157	0,206	0,258	$-7788/T + 3,707$	35,82	5,936
15	0,078	0,112	0,155	0,202	0,250	$-7776/T + 3,691$	35,80	5,816
16	0,085	0,118	0,163	0,214	0,272	$-7848/T + 3,757$	36,88	6,352
17	0,075	0,111	0,153	0,200	0,249	$-7776/T + 3,687$	35,79	5,834
18	0,081	0,113	0,156	0,203	0,252	$-7697/T + 3,654$	35,47	6,013
19	0,068	0,099	0,142	0,191	0,242	$-8636/T + 4,152$	39,77	5,886
20	0,090	0,128	0,188	0,254	0,349	$-9030/T + 4,955$	41,66	7,892
21	0,064	0,123	0,181	0,247	0,343	$-9182/T + 4,571$	42,00	7,886
22	0,089	0,126	0,185	0,253	0,347	$-9152/T + 4,565$	41,90	8,107
23	—	—	0,126	0,238	0,320	$-8533/T + 4,185$	39,03	7,599
24	0,063	0,089	0,128	0,167	0,215	$-8303/T + 3,906$	38,15	5,082
25	0,076	0,094	0,138	0,183	0,230	$-8758/T + 4,201$	40,36	5,449
26	0,066	0,092	0,131	0,175	0,226	$-8455/T + 4,012$	38,85	5,366

elektrischen Leitfähigkeitsmessungen wird in Zahlentafel 3 gegeben. Die Auftragung der  $\log \alpha$ -Werte in Abhängigkeit von der reziproken absoluten Temperatur in Bild 10 zeigt, daß die Leitfähigkeits-Temperatur-Beziehungen aller untersuchten Schmelzen linear verlaufen und demgemäß dem Gesetz für unipolare Leitung von Rasch u. Hinrichsen [20]:

$$\alpha = A \cdot e^{-\Delta E/RT} \text{ bzw. } \log \alpha = -\Delta E/4,575 T + C$$

entsprechen. Es bedeuten:  $\alpha$  = spez. elektrische Leitfähigkeit,  $\Delta E$  = Ablösearbeit oder Aktivierungsenergie,  $R$  = Gaskonstante,  $T$  = absolute Temperatur,  $A$  und  $C$  = Konstante.

Aus der Steigung der Leitfähigkeits-Temperaturgeraden läßt sich die Ablösearbeit berechnen, die ein Maß darstellt für die zur Ionenbewegung erforderliche Energie. Sie wird im schmelzflüssigen Zustand bekanntlich durch die Größe und Ladung der stromtransportierenden Ionen sowie deren gegenseitige Beeinflussung bestimmt. Die aus dem Kurvenverlauf bestimmte Temperaturabhängigkeit des elektrischen Leitvermögens der Schmelzen sowie die Werte für die Ablösearbeiten sind zusammen mit der aus den Versuchsergebnissen der Dichte- und Leitfähigkeitsmessungen für 1550 °C berechneten molaren Leitfähigkeit  $A_m$  [ $\text{cm}^2/\Omega \cdot \text{mol}$ ] in Zahlentafel 3 aufgeführt.

Über die Abhängigkeit der elektrischen Leitfähigkeit von der Schlackenzusammensetzung gibt eine in Bild 11 wiedergegebene Zusammenstellung der bisher vorliegenden Meßwerte bei 1550 °C Aufschluß. Die im Diagramm näherungsweise eingetragenen Linien gleichen elektrischen Leitvermögens lassen erkennen, daß die Iso-Leitfähigkeitskurven in dem untersuchten Konzentrationsbereich nahezu parallel zu den CaO-Konzentrationsgeraden des Systems verlaufen. In einer Dreiecksdiagramm-Darstellung ergibt sich demgemäß

ein paralleler Verlauf zum Randsystem Al<sub>2</sub>O<sub>3</sub> – SiO<sub>2</sub>. Aus dieser Leitfähigkeitskonzentrations-Abhängigkeit wird deutlich, daß das elektrische Leitvermögen der

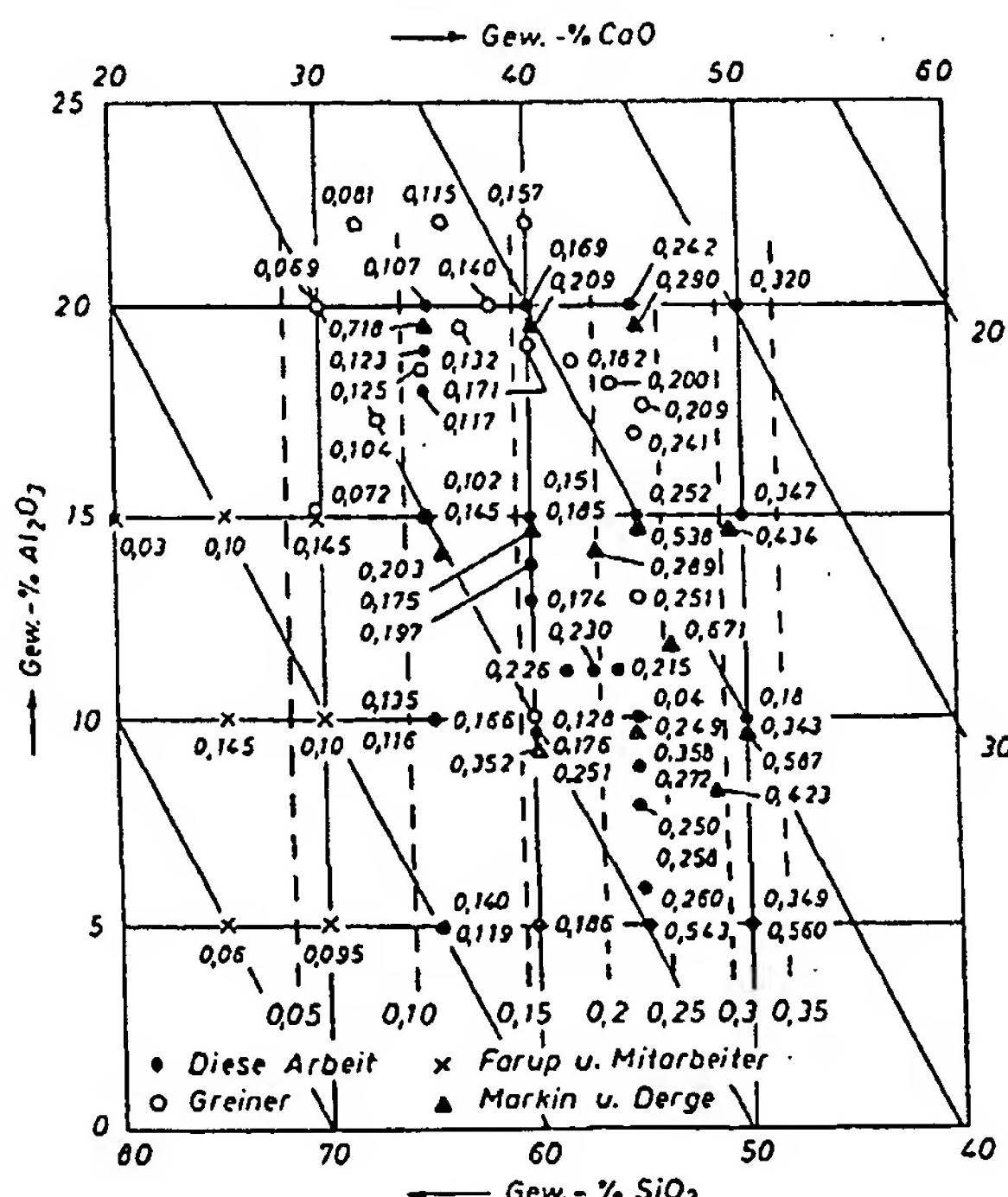


Bild 11. Linien gleicher elektrischen Leitvermögens bei 1550 °C im Dreiecksdigramm des Systems CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>

Kalk-Tonerde-Silikate im schmelzflüssigen Zustand hauptsächlich vom CaO-Gehalt bestimmt wird, d. h., daß der Stromtransport im wesentlichen durch freie

Kalziumionen erfolgt. Eine ähnliche Konzentrations-abhängigkeit der Schmelzeigenschaften dieses Systems lassen auch die Linien gleicher Viskosität [21] erkennen. Den Versuchsergebnissen ist ferner zu entnehmen, daß das Leitvermögen der Schlacken mit sinkenden Kieselsäuregehalten und abnehmender Verhältniszahl von  $\text{Al}_2\text{O}_3/\text{CaO}$  zunimmt.

Ein Vergleich der verschiedenen Meßwerte zeigt, daß einige der von Farup, Fleischer u. Holtan [3] mit einer verhältnismäßig einfachen Versuchseinrichtung bestimmten elektrischen Leitfähigkeitswerte gut mit den Ergebnissen der vorliegenden Untersuchungsreihe übereinstimmen. Markin u. Dergé [4] geben demgegenüber meist wesentlich höhere Leitfähigkeitswerte an. Diese Abweichungen dürften vielleicht damit zu erklären sein, daß bei der von den Autoren gewählten Anordnung von Elektroden und Tiegel ein Teil des Stromes durch den stark leitenden Tiegel fließt und somit der gemessene Badwiderstand kleiner erscheint.

Abweichend von dem stetigen Verlauf der Dichte-Konzentrationsbeziehungen der untersuchten Kalk-Tonerde-Silikate wurde in Übereinstimmung mit den Versuchswerten von Hofmann u. Marincek [5] bei den Leitfähigkeitsmessungen eine schwach ausgeprägte Zunahme des Leitvermögens bei Schmelzen mit 46% SiO<sub>2</sub> festgestellt. Als Beispiel für dieses

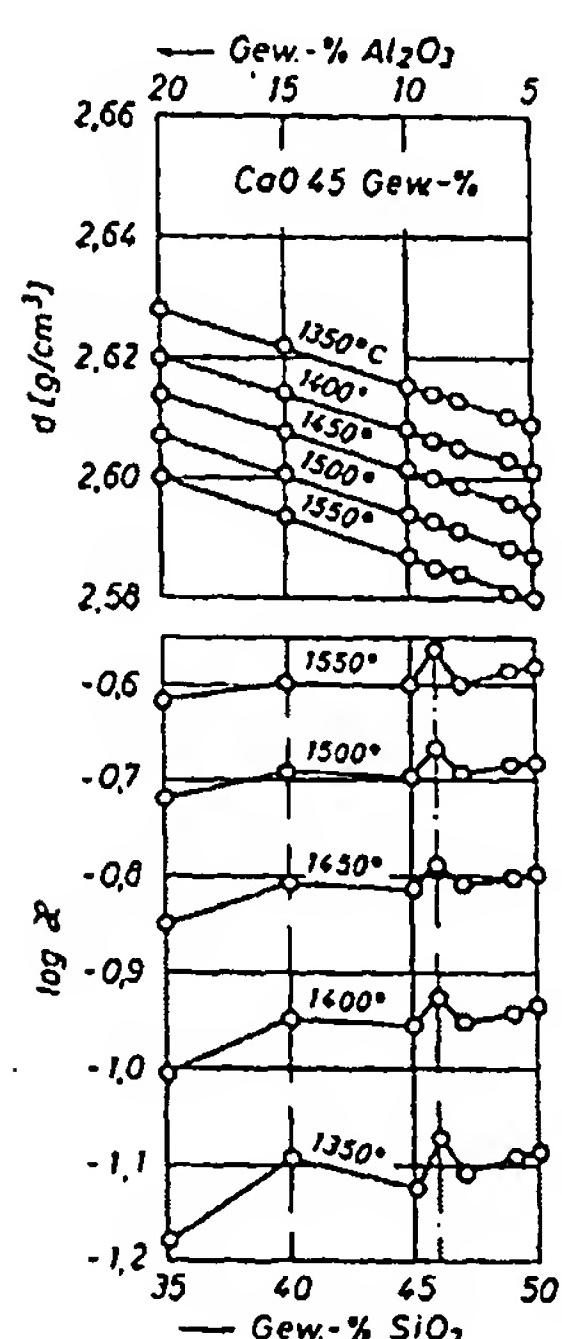


Bild 12. Elektrische Leitfähigkeit und Dichte von Schlacken mit konstantem CaO-Gehalt in Abhängigkeit von der  $\text{Al}_2\text{O}_3$ - und  $\text{SiO}_2$ -Konzentration

den bereits ausführlicher in den Arbeiten I bis IV behandelt.

Eine lineare Leitfähigkeits-Schlackenkennzahl-Beziehung mit geringem Streubereich ergibt sich — wie aus Bild 13 ersichtlich wird — bei der Auftragung der Leitfähigkeits-Meßwerte in Abhängigkeit vom Verhältnis

der sog. Netzwerkswandler (Kationen ohne glasbildende Eigenschaften, wie z. B.  $\text{Ca}^{2+}$ ) zu den Netzwerksbildnern ( $\text{Si}^{4+}$ ,  $\text{Al}^{3+}$ )

$$K_{\text{ZI}} = \frac{I_{\text{Kat}} \cdot \text{At.\% Kat}}{(I_{\text{Si}} \cdot \text{At.\% Si}^{\text{d}}) \cdot (I_{\text{Al}} \cdot \text{At.\% Al}^{\text{d}})}$$

unter Einbeziehung der Sauerstoffionen-Attraktion / [22, 23].

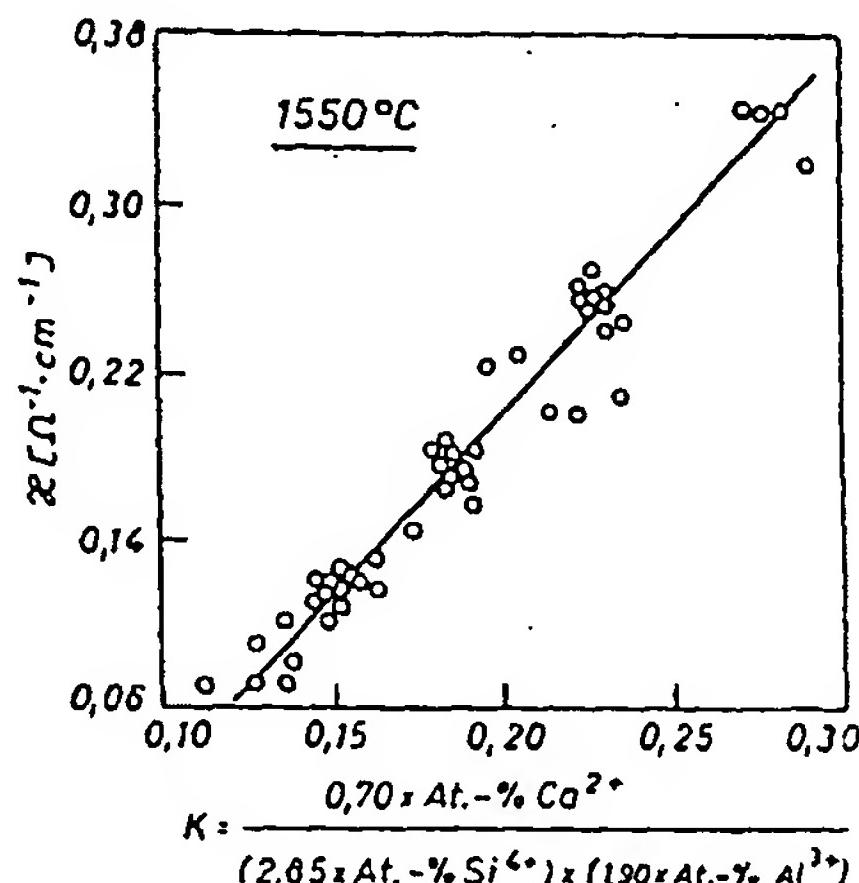


Bild 13. Leitfähigkeits-Kennzahl-Beziehungen der Kalk-Tonerde-Silikatschmelzen

Der Parameter  $J$  wird definiert durch die Beziehung

$$I = \frac{n \cdot e^2}{R}$$

( $n$  = Wertigkeit des Kations;  $e$  = el. Ladung;  $R$  = Kationenradius) und ist ein Maß für die Bindungs-kräfte zwischen den Kationen und Sauerstoffionen (M-O-Bindungen) bzw. den Wechselwirkungen zwischen

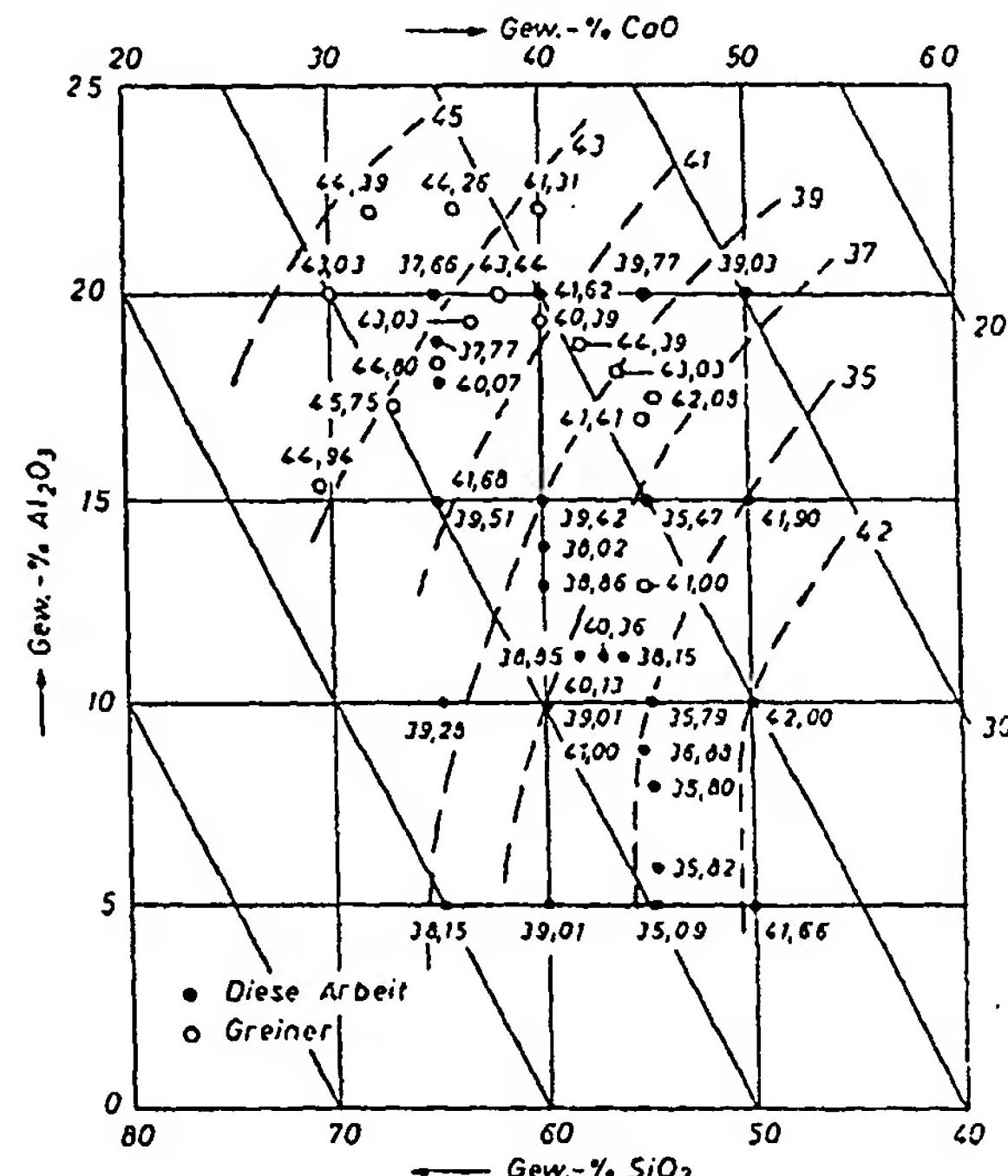


Bild 14. Abhangigkeit der Aktivierungsenergie von der Schlackenzusammensetzung bei 1550 °C

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Kationen und dem Silikatnetzwerk. Infolge der relativ großen Sauerstoffionen-Attraktion der Erdalkali-Ionen sind bei geringen Gehalten dieser Kationen in den Schmelzen zur Überwindung der M-O-Bindungskräfte in den Silikaten hohe Aktivierungsenergien erforderlich. Mit steigender Konzentration der Kationen ohne glashildende Eigenschaften wird — wie aus der Wiedergabe der berechneten Aktivierungsenergien im System  $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$  zu ersehen ist (Bild 14) — durch den fortschreitenden Abbau des Silikatnetzwerkes die zur Ionenbewegung erforderliche Aktivierungsenergie geringer. Der im Diagramm zu beobachtende Anstieg der Aktivierungsenergien im Bereich hoher CaO-Gehalte dürfte vermutlich mit der höheren Liquidustemperatur dieser Schmelzen zusammenhängen.

### Zusammenfassung

In den vorliegenden Versuchsreihen wurden im Temperaturbereich von 1350 bis 1550 °C die Dichte und elektrische Leitfähigkeit von 26 Schlackenschmelzen des Systems  $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$  im Konzentrationsbereich 35 bis 60 % CaO, 5 bis 20 %  $\text{Al}_2\text{O}_3$  und 30 bis 60 %  $\text{SiO}_2$  bestimmt.

Die Versuchsergebnisse der Dichtemessungen zeigen eine lineare Temperaturabhängigkeit sowie eine stetige Konzentrationsabhängigkeit.

Die Dichte der Schlacken nimmt mit abnehmenden  $\text{SiO}_2$ -Gehalten bzw. steigenden CaO- sowie  $\text{Al}_2\text{O}_3$ -Konzentrationen zu und wird maßgeblich vom Verhältnis  $\text{SiO}_2/\text{CaO}$  in den Schmelzen bestimmt.

Den Bestimmungen der elektrischen Leitfähigkeit ist zu entnehmen, daß das Leitvermögen der  $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ -Schmelzen hauptsächlich vom CaO-Gehalt der Schmelzen abhängt. Eine stärkere Leitfähigkeitszunahme wurde im Konzentrationsbereich der Verbindung  $\text{CaO}\cdot\text{SiO}_2$  festgestellt. Für alle Schmelzen ergibt sich eine lineare Temperaturabhängigkeit der log  $\alpha$ -Werte.

Herrn Dipl.-Ing. F. Gaßner, der im Rahmen seiner Diplomarbeit die vorliegenden Untersuchungen durchführte, danken wir an dieser Stelle.

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## Vom Allgemeinen Landrecht zum Allgemeinen Berggesetz\*)

Von Prof. Dr. jur. Raimund Willecke, Clausthal-Zellerfeld

*Vor 100 Jahren, am 24. Juni 1865, wurde das „Allgemeine Berggesetz für die Preußischen Staaten“ verkündet. Aus diesem Anlaß gibt der Verfasser einen Abriß der Entstehung des Gesetzes. Zunächst wird der vorher bestehende Rechtszustand im rechtsrheinischen Gebiet des deutschen Bergrechts, das auf den alten Bergordnungen, dem Allgemeinen Landrecht und dem gemeinen deutschen Recht beruhte, und im linksrheinischen Gebiet des seit 1801 geltenden französischen Bergrechts geschildert. Versuche einer Umgestaltung und Vereinheitlichung der nur noch schwer übersehbaren Rechte blieben in den Jahren 1826 bis 1850 noch erfolglos, so daß man sich mit der sog. Novellengesetzgebung behelfen mußte. Von 1861 an führte dann der an den Oberbergrat, späteren Berghauptmann Hermann Brassert erteilte Auftrag über einen „Vorläufigen“ und einen endgültigen Entwurf, deren voneinander abweichende Grundsätze vom Verfasser dargelegt werden, zum Allgemeinen Berggesetz.*

Der von Berghauptmann Brassert auf dem deutschen Bergmannstag in Kassel im Jahre 1880 vorgebrachte Wunsch einer Vereinheitlichung des gesamten deutschen Bergrechts, der bisher niemals verwirklicht

\*) Vortrag vor dem Geschichtsausschuß der Gesellschaft Deutscher Metallhütten- und Bergleute am 15. Juni 1964 in Bochum.

worden ist, hat in jüngster Zeit wieder Auftrieb bekommen durch das Drängen des Bergbaus nach einem einheitlichen Bundesberggesetz. Wenn heute die Vorarbeiten für ein Bundesberggesetz anlaufen, so darf es einer Betrachtung wert sein, aufzuzeigen, welche Schwierigkeiten auf gesetzlichem Wege zu beseitigen

Ti at least 4% C and  $\leq 2$ , and B 0.003–0.005%. The B is added to improve the hot workability, and 0.1–0.3% misch metal can be substituted for it but gives a dirtier steel. The Nb or Ti is used only to prevent intergranular corrosion after welding. The Cr, Ni, Mo, and Cu contents are crit. for prevention of stress corrosion cracking in  $H_2SO_4$ . Forged bars of a steel contg. C 0.054, Mn 0.91, Si 0.51, Cr 20.57, Ni 32.68, Mo 2.32, Cu 3.28, N 0.039, Nb plus Ta 0.81, and B 0.006% were machined  $\frac{1}{8} \times \frac{1}{8} \times 3.75$  in. and bent cold around a 1-in. round bar, bolted to U shape, and immersed in boiling 30–40%  $H_2SO_4$  not aerated, for 330 hrs. without cracking. A Ti-stabilized steel contg. only 30.03% Ni but otherwise within the specified compn. range, prep'd. and tested similarly, cracked in 24–135 hrs.

George F. Comstock

Pearlitic cast iron containing antimony. Heinrich Teves, Ernst A. Teves, and Martin Tausend (trading as Alfred Teves Maschinen- und Armaturenfabrik K.-G.). Brit. 980,361 (Cl. C 21b), Jan. 13, 1965; Ger. Appl. Nov. 2, 1961; 2 pp. Pearlitic cast iron free from ferrite is produced by adding 0.1% Sb, preferably in the ladle or mold before pouring the molten iron. Cementite formation in chilled castings is decreased, the graphite flakes are coarsened, and the hardness and other mech. properties are improved by the Sb. Suitable compns. for the Sb treatment are C 2.8–3.7, Si 1.8–2.8, Mn 0.4–1.2, P 0.15–0.8, and S 0.04–0.18%.

George F. Comstock

Complex arsenic compound acts as corrosion inhibitor in aqueous ammoniacal solutions. Bernard C. Creech, Lawrence V. Collings, and Paul Shapiro (to Sinclair Research, Inc.). U.S. 3,168,392 (Cl. 71–59), Feb. 2, 1965, Appl. Aug. 28, 1961; 3 pp. Ammonium solns. are normally stored in Al containers because of the passivity of the oxide layer. In order to utilize steel containers, gluconic acid,  $As_2O_3$ , and  $NH_4$ , or metal hydroxides were caused to react to form a novel corrosion inhibitor for these nitrogen solns.: 10.157 g.  $As_2O_3$ , 10 g. 28–30%  $NH_4OH$ , and 30.01 g. 50% gluconic acid soln. were mixed and heated to 190°F. and refluxed for one hr. The soln. was a clear dark brown liquid, sp. gr. 1.389, with an As content of 15.98 wt. %. This new compd. was more sol. in ammoniacal  $NH_4NO_3$  than  $As_2O_3$ , esp. where the  $NH_4$ /water ratio was  $\geq 1.5$ . KOH may be substituted for the  $NH_4OH$  in the reaction for prep. a similar corrosion inhibitor. Only gluconic acid of similar org. compds. produces a compd. having an As solv. in N solns.  $> 0.05$  wt. %. Mild steel coupons  $3 \times \frac{1}{8} \times \frac{1}{16}$  in. were pickled in 15% HCl at 150°F. until H bubbles were evolved. These coupons were rinsed and partially or wholly submerged for 30 days in 100 ml. ammoniacal solns. contg. 0.065% As as the complex As compd. together with 0.125%  $CuCO_3 \cdot Cu(OH)_2$  and 0.085%  $NaNO_2$  (vapor phase inhibitor). The strips remained passive and bright for the entire period. Other tests were performed such as touching the steel with a Cu wire and passing current through the bimetallic cell to try to disrupt the film and scratching the passive coupon; the coupons remained passive.

R. L. Littler

Corrosion inhibition. Associated Octel Co. Ltd. Fr. 1,357,359 (Cl. C 10), April 3, 1984; Brit. Appl. June 6, 1962; 5 pp. Corrosion of Fe by additives such as ethylene dibromide and Pb alkyls and by petroleum stocks contg. them is inhibited by addn. of  $\leq 1$  vol. % epichlorohydrin to the additive. iso-Bu or *tetra*-Bu acetate may also be added.

N. D. Clare

Antirust layer on iron or steel. Hermann Wiederhold, Lacksfabriken (by Hans Sagel). Ger. 1,184,679 (Cl. B 44d), Dec. 31, 1964, Appl. Oct. 17, 1956; 2 pp. Iron or steel surfaces are coated with org. primings, esp. polystyrene (I) alone or mixed with silicone resin, of high contents of Zn dust (particle diam. 2–5  $\mu$ ), and subjected to min. 420° under spontaneous oxidn. to ZnO particles of larger vol. The coatings may be thermally exposed up to at least 700° without destruction and loss of their rustproofing. For example, a sand-blasted steel plate was cold coated by electrostatic spraying with a priming composed of 25% soln. of I in xylene 15.4, Zn dust 73.1, suspended matter 1.7, naphtha, 2.5, and xylene 7.3 parts. After airing the treated plate was exposed for 1 hr. to 700–50° in a muffle furnace.

Hans Meyer

Alloy steels resistant to corrosion, tempering, and softening at g

high temperatures. Birger L. Johnson, Jr. (to Latrobe Steel Co.). U.S. 3,167,423 (Cl. 75–120), Jan. 26, 1965, Appl. April 14, 1964; 3 pp. Steels resistant to corrosion, and having greater hot hardness than conventional stainless steels, contain C 1.1–1.2, Mn 0.4–0.6, Si 0.2–0.4, Cr 14–16, Mo 3.5–4.5, V 1–2, and P and S each 0.025% max. The steels are hardened by oil-quenching from 2000°, tempering 2 hrs. at 1000°F., refrigerating at –100°F., and tempering similarly again. Hot hardness tests, and room-temp. hardness after tempering at various temps. up to 1000°F., in comparison with steels contg., resp., C 1.05, Cr 17.25, and Mo 0.5%, and C 0.8, Cr 4.1, Mo 4.25, and V 1.1%, show the V-bearing 14–16% Cr steel superior to the others in both respects, and it is highly resistant to corrosion. It shows max. hardness after tempering at about 950°F., instead of 950°F. as does the other stainless steel lacking V. The steels are specially suitable for bearings operating at high temps.

George F. Comstock

Poly(vinyl butyral) binder for brazing powders. Jerome A. Berson and Arthur T. Cape (to Powder Melting Corp.). U.S. 3,166,402 (Cl. 75–5), Jan. 19, 1965, Appl. Sept. 24, 1963; 2 pp. In the application of powd. brazing alloys contg. chiefly Cu, Ni, Co, or Mn to metallic parts to be brazed, a binder that is easily suspended in  $H_2O$  can form with the powder a flexible partially dried shape such as a strip or washer for application to the joint, and on heating to the 1700–2150°F. brazing temps. evap. without residue, is poly(vinyl butyral), which is superior to other polyvinyl compds. The preferred mixt. is 3 parts metallic powder to 1 of a 32.5% aq. suspension of the compd. by wt., and dried shapes for application in brazing should contain 8% poly(vinyl butyral) and 2%  $H_2O$  by wt. The balance may be composed of powd. alloy contg. Ni 82, Cr 7, Si 5, B 3, and Fe 3%, but many other alloy powders are suitable. The compn. is esp. useful for brazing stainless steels and heat-resistant alloys.

George F. Comstock

Welding nodular cast iron. International Nickel Ltd. Brit. 980,614 (Cl. C 22c), Jan. 13, 1965; Ger. Appl. Feb. 11, 1961; 2 pp. Cast iron having graphite in the spheroidal form can be gas-welded, without requiring subsequent annealing to prevent hard carbide formation in or near the weld, if it contains C 3–4.2, Si 2.5–3, Mn and P  $\leq 0.1$  each, Mg 0.04–0.08%, and no Cr or Mo, if it can be sand-cast entirely ferritic in sections 10 mm. thick, if the filler rod is composed of the same alloy, and the parts to be welded are preheated. When 2 plates of cast iron having spheroidized graphite and contg. C 3.9, Si 2.5, P 0.03, Mn 0.008, and Mg 0.055%, were preheated to 200° and oxy-acetylene welded with rods of the same compn. to form a single-V butt weld, the joint was free from hard phases, had 84 kg./mm.<sup>2</sup> tensile strength, 6% elongation, 290 max. Brinell hardness, and 20° bend breaking angle.

George F. Comstock

Welding ferritic nickel steels. International Nickel Ltd. (by James V. Peck). Belg. 637,650, March 20, 1964; Brit. Appl. Sept. 21, 1962; 14 pp. In a process for elec. arc welding under protective gas of articles consisting of ferritic Ni steel contg. Ni 8–20, and C 0.03–0.2, the welding material (welding rod) used contains Ni 11–15, C 0.001–0.07, Si  $\leq 1$ , Mn  $\leq 6$ , Al  $\leq 0.15$ , S  $\leq 0.02$ , P  $\leq 0.02$ , Mo  $\leq 0.3\%$ , remainder Fe and impurities. The welding material may also contain Ti 0.05–0.15%. It contains <200 ppm. O, <100 ppm. N, and <3 ppm. H.

Friedrich Epstein

See also: Analytical Chemistry, Section 2. Electrochemistry, Section 15. Extractive Metallurgy, Section 18. Nonferrous Metals and Alloys, Section 20. Solving equations of ternary diffusion (Kirkaldy) 3. Measurement of dew-point of flue-gases and its effect on the start of corrosion (Roegener) 3. Thermoelec. properties of acid slags (Kalmykov) 9. Chem. engineering aspects of L.D. (Linz-Donawitz Process) and assocd. processes (Grainger) 16. Measurements and control problems in neutralization and depoisoning of waste water (Suess) 23. Electrochem. purification of cyanide waste water (Komendova) 23. Localized corrosion during chem. cleaning (Rice) 24. Development and evaluation of lubricant composite materials (contg. powd. metals) (Campbell) 27.

Patent: Metalworking lubricants (Kolarik) 27.

## 20—NONFERROUS METALS AND ALLOYS

DANIEL J. MAYKUTH

Metals for cryogenic applications. Pierre Vachet. Rev. Aluminium 41(326), 1283–97(1964)(Fr). A review of the mechanical properties and weldability of selected steels, Al alloys, Ti alloys, Cu alloys, and Ni alloys. 19 references.

A. Matte

Structure and properties of metallurgical slags. V. Density determinations and electrical conductivity measurements on melts in the system lime-alumina-silica. Roland Kammler and Helmut Winterhager (Tech. Hochschule, Aachen, Ger.). Z. Erzbergbau Metallhuettenw. 18, 9–17(1965)(Ger); cf. CA 56, 2185, 3152h. D. and elec. cond. of 26 slags in the system  $CaO-Al_2O_3-SiO_2$ .

$SiO_2$ , contg.  $CaO$  35–80,  $Al_2O_3$  5–20, and  $SiO_2$ , 30–60% were detd. at 1350–1550°. D. shows a linear temp. dependence as well as a steady concn. dependence. The d. of the slags increases with decreasing  $SiO_2$  and rising  $CaO$  and  $Al_2O_3$  concns. and is proportional to the ratio  $SiO_2/Al_2O_3$  in the melts. The elec. cond. of these molten slags depends principally on their  $CaO$  content. A marked cond. increase occurs in the concn. range of the compd.  $CaO \cdot SiO_2$ . Detailed measurements are tabulated and shown in graphs. 23 references.

H. Stoertz  
Aluminum casting alloys and properties. Edward Treloar (Apex Smelting Co., Cleveland, Ohio). Mod. Castings, New

**EXHIBIT E**

Table 4 - 16 Viscosities of  $\text{Al}_2\text{O}_3$  ternary systems.

$\text{Al}_2\text{O}_3-\text{M}_2\text{O}-\text{SiO}_2$			viscosity (P) at given temperature ( $^{\circ}\text{C}$ )					Ref.		
$\text{Li}_2\text{O}$	$\text{Al}_2\text{O}_3$	$\text{SiO}_2$	1250	1300	1350	1400	1400			
30	5	65	99.3	71.7	52.8	39.6	39.6	042		
35	5	60	42.3	30.9	23.1	17.5	17.5			
40	5	55	15.8	12.47	9.99	8.10	8.10			
45	5	50	14.87	10.65	7.91	5.80	5.80			
50	5	45	5.94	4.69	3.76	3.06	3.06			
30	10	60	102.3	69.7	48.6	34.6	34.6			
35	10	55	49.1	36.3	27.3	20.9	20.9			
40	10	50	23.2	17.4	13.30	10.31	10.31			
45	10	45	12.97	9.69	7.37	5.69	5.69			
25	15	60			114.2	85.7	85.7			
30	15	55		104.7	70.1	48.1	48.1			
35	15	50	55.1	40.7	30.6	23.4	23.4			
40	15	45	25.0	18.0	13.24	9.91	9.91			
30	20	50			64.2	43.7	43.7			
$\text{Na}_2\text{O}$										
20	5	75				( 136/1500 )	040			
30	5	65	168	117	82.7	59.8	59.8	read		
40	5	55	50.1	34.1	23.7	16.9	16.9	from graph		
20	10	70				( 252/1500 )	graph			
25	10	65				213				
30	10	60			165	114	114			
35	10	55	224	144	95.3	64.6	64.6			
40	10	50	84.9	57.8	40.3	28.8	28.8			
50	10	40	20.9	15.0	11.0	8.23	8.23			
30	20	50				( 192/1500 )				
$\text{K}_2\text{O}$										
32.5	2.5	65			143.8	100.5	100.5	042		
37.5	2.5	60	119.3	87.2	65.1	49.4	49.4			
42.5	2.5	55	42.4	30.3	22.1	16.4	16.4			
35	5	60		168.9	117.3	83.3	83.3			
40	5	55	112.6	75.6	52.0	36.6	36.6			
45	5	50	37.1	30.2	24.9	20.7	20.7			
50	5	45	20.5	14.6	10.6	7.86	7.86			
37.5	7.5	55		194.5	127.3	85.4	85.4			
42.5	7.5	50	118.0	72.9	46.3	30.3	30.3			
40	10	50			151.3	103.2	103.2			
45	10	45	107.4	68.1	44.3	29.7	29.7			
50	10	40	60.4	43.3	31.7	23.6	23.6			
$\text{Al}_2\text{O}_3-\text{MoO}_3-\text{SiO}_2$			log viscosity (P) at given temperature ( $^{\circ}\text{C}$ )							
wt. % of oxide*)	$\text{CaO}$	$\text{Al}_2\text{O}_3$	1150	1200	1250	1300	1350	$\log_{10}$		
		$\text{SiO}_2$						Ref.		
	45	20	35				1.134	0.881	0.695	043
	40	25	35				1.299	1.076	0.877	
	35	30	35				1.501	1.276	1.064	
	30	35	35		2.394	2.037	1.738	1.497	1.279	
	25	40	35					1.612	1.396	
	50	10	40				0.921	0.719	0.603	
	45	15	40		1.933	1.605	1.346	1.124	0.915	0.713
	40	20	40		2.155	1.830	1.545	1.332	1.137	0.920
	35	25	40		2.452	2.107	1.806	1.543	1.336	1.155
	30	30	40				2.111	1.841	1.597	1.433

\*) by batch

 $\partial \log ( )$

$\text{Al}_2\text{O}_3$ - $\text{Mo}$ - $\text{SiO}_2$  ( cont. )

wt.% of oxide *)			log viscosity (P) at given temperature ( $^{\circ}\text{C}$ )								Ref.
CaO	$\text{Al}_2\text{O}_3$	$\text{SiO}_2$	1150	1200	1250	1300	1350	1400	1450	1500	
50	5	45							0.681	0.533	043
45	10	45					1.064		0.879	0.688	
40	15	45				1.520	1.288	1.100	0.931		
35	20	45	2.829	2.435	2.097	1.801	1.569	1.354	1.176		
30	25	45				2.121	1.846	1.613	1.420		
25	30	45							1.848		
45	5	50							0.679		
40	10	50				1.283		1.083	0.915		
35	15	50	3.097	2.671	2.320	2.021	1.757	1.540	1.340	1.155	
30	20	50		2.723	2.393	2.097	1.851	1.626	1.480		
25	25	50						1.999	1.761		
40	5	55						1.107	0.924		
35	10	55			2.068	1.784	1.553	1.348	1.179		
30	15	55	3.444	3.033	2.659	2.352	2.083	1.865	1.651	1.456	
25	20	55	3.900	3.458	3.079	2.763	2.490	2.233	1.688	1.789	
20	25	55					2.820	2.501	2.238		
35	5	60					1.596	1.398	1.233		
30	10	60	3.401	2.996	2.624	2.342	2.100	1.912	1.713	1.513	
25	15	60	4.025	3.572	3.193	2.863	2.592	2.330	2.107	1.890	
20	20	60		4.167	3.760	3.403	3.100	2.822	2.548	2.310	
15	25	60					3.398	3.086	2.793		
30	5	65						1.844	1.625		
35	10	65	4.045	3.619	3.250	2.931	2.663	2.408	2.182	1.976	
20	15	65				3.653	3.292	3.017	2.759	2.493	
15	20	65			4.494	4.167	3.809	3.507	3.201	2.973	
10	25	65						3.598	3.279		
20	10	70					3.029	2.778	2.558		
15	15	70		5.212	4.754	4.346	3.994	3.671	3.378	3.121	
10	20	70			5.107	4.665	4.260	3.918	3.597		

170°  
213  
1973

wt.% of oxide *)			viscosity (P) at given temperature ( $^{\circ}\text{C}$ )								Ref.
CaO	$\text{Al}_2\text{O}_3$	$\text{SiO}_2$	1450	1500	1550	1600	1700	1800	1900	2000	
60	30	10		2.2 ✓	1.2 ✓	0.8	0.6	0.4			002
50	40	10	7.7	5.0 ✓	3.3 ✓	2.3 ✓	1.5	1.0	0.8		
40	50	10			5.2 ✓	3.4 ✓	1.7	1.2	1.0		
35	55	10				3.9 ✓	1.9	1.4			
25	65	10					1.7	1.2			
50	30	20 ✓				2.4 ✓	1.4	1.0	0.7	0.6	
40	40	20 ✓			6.3	4.0 ✓	2.0	1.3	0.9		
30	50	20 ✓	11.5		7.4 ✓	4.7 ✓	2.5	1.5	1.2	1.0	
20	60	20					2.7	1.6	1.3		
50	20	30				2.5 ✓	1.4	0.9	0.7	0.6	
40	30	30	9.2		6.1	4.4 ✓	2.4	1.5	1.3	1.1	
30	40	30	30.2	18.0	11.4 ✓	7.8 ✓	4.4	2.4	1.7	1.2	
20	50	30					5.0	3.0	1.8	1.2	
10	60	30	5.23						1.9	1.2	
50	10	40	5.3	3.9	2.8 ✓	2.1 ✓	1.3	1.0	0.8	0.6	
40	20	40	14.7	9.2	6.2 ✓	4.3 ✓	2.2	1.8	1.4	1.2	
30	30	40	39.2	25.7	16.8 ✓	11.0 ✓	5.3	2.8	2.0	1.6	
20	40	40	39.5		19.9 ✓	9.6	5.3	3.1			
20.2	36.6	43.2			25.4 ✓	10.7		5.6			
40	10	50 ✓	12.3	8.6 ✓	6.2 ✓	4.5 ✓	2.6	1.8	1.4	1.0	
30	20	50	42.4	32.2	22.1 ✓	15.8 ✓	8.4	4.4	3.0	2.5	
20	30	50	42.2			22.3	10.7	6.0	3.8		
10	40	50					12.4	6.1	3.7		
30	10	60			17.9	8.9	5.0	3.0			
20	20	60			38.0	18.7	10.1	7.3			
10	30	60				25.5	12.4				

\*) by batch.

in percent values from Ref 43

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# **Handbook of Physico-chemical Properties at High Temperatures**

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**and  
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The Iron and Steel Institute of Japan

**EXHIBIT F**

# Phase Diagrams for Ceramists

Ernest M. Levin,  
Carl R. Robbins and  
Howard F. McMurdie

Compiled at the National Bureau of Standards

Margie K. Reser, Editor

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### *Three Oxides*

Fig. 630

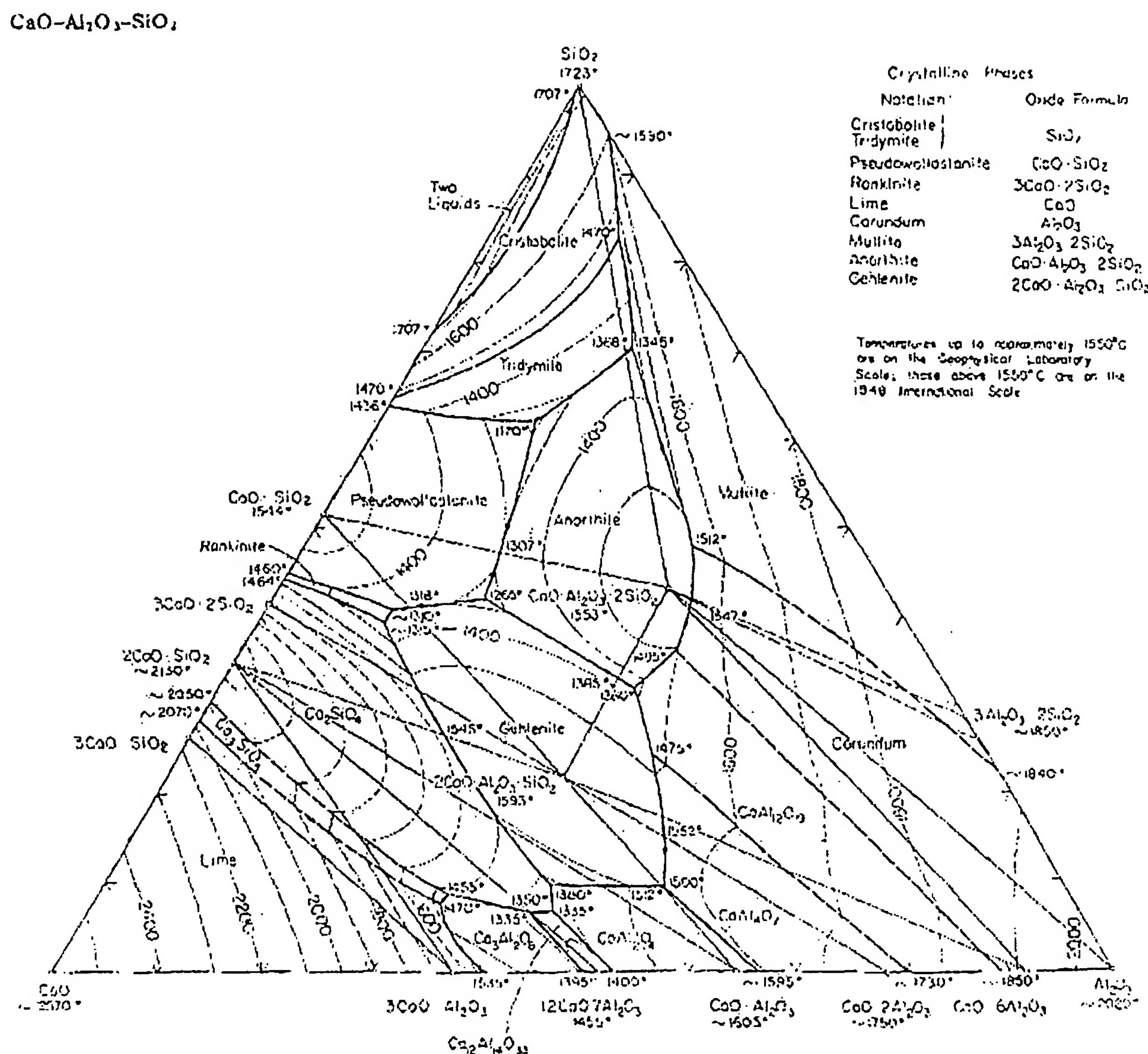


Fig. 6-30. Sintered  $\text{CaO}\cdot\text{Al}_2\text{O}_5\cdot\text{SiO}_2$  composite.

E. F. Osborn and Arnold Moran, revised and redrawn "Phase Equilibrium Diagrams of Oxide Systems," Plate I, published by the American Ceramic Society and the Edward Orton, Jr., Ceramic Foundation, 1950.

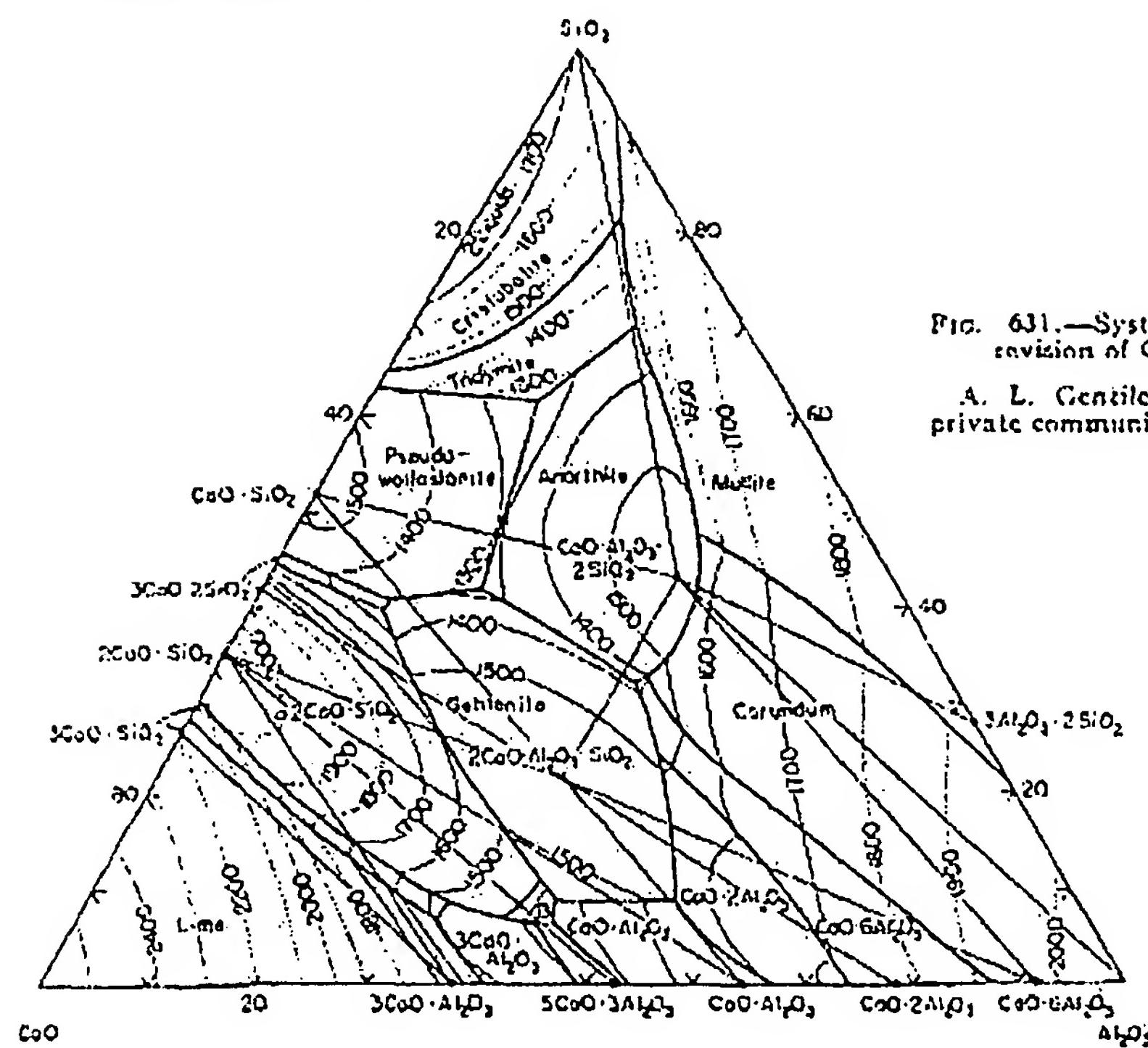
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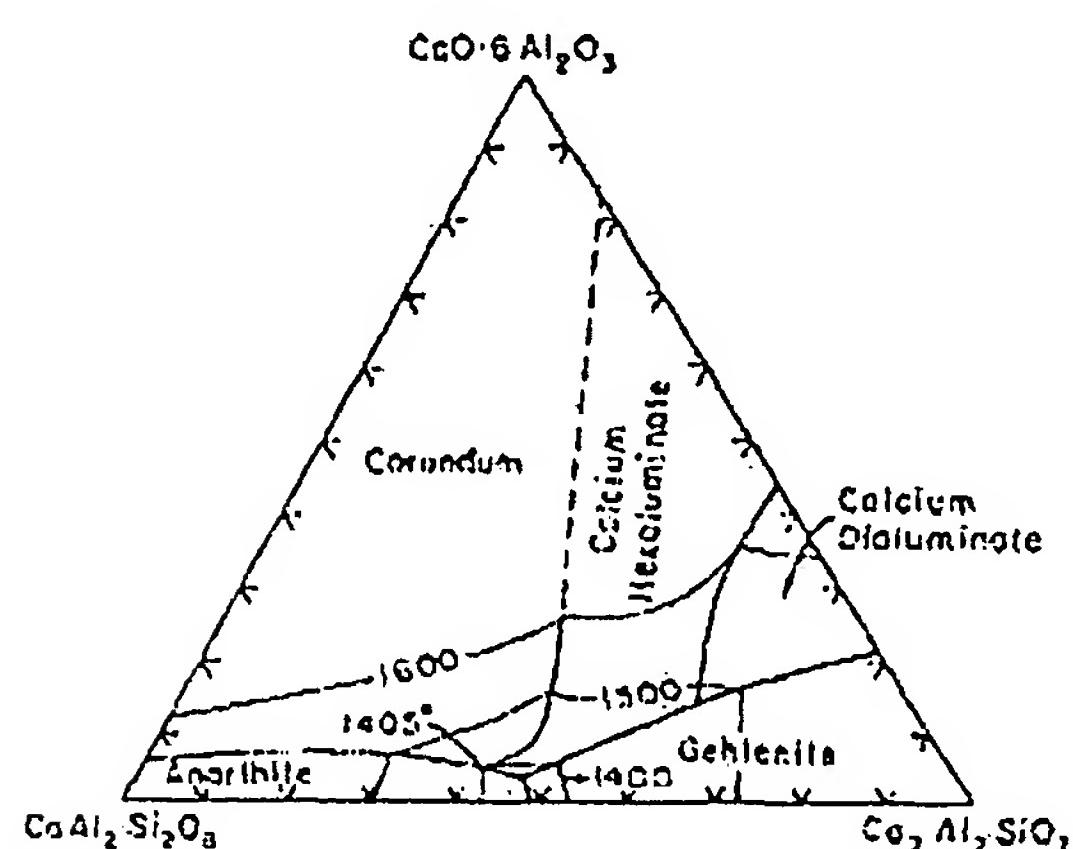
Figs. 631-634

220

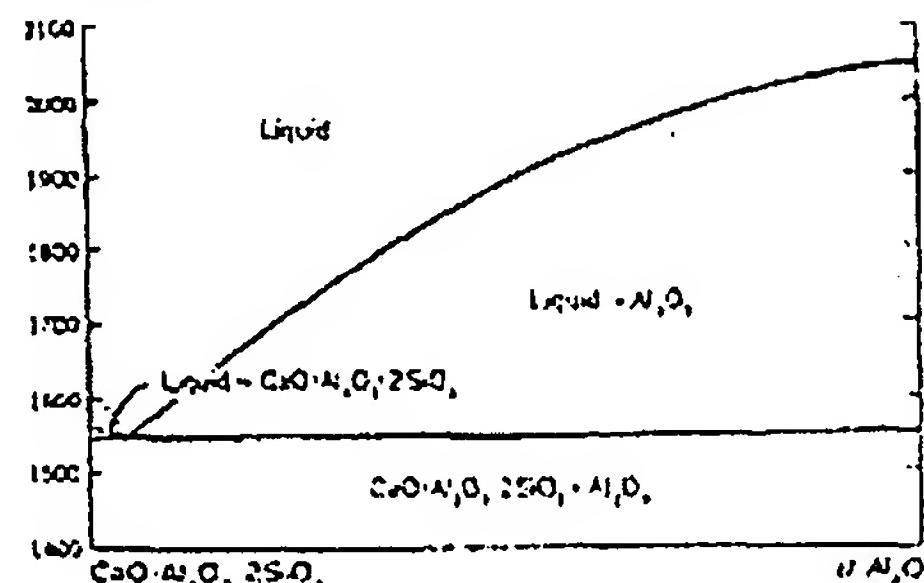
Metal Oxide Systems

 $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  (cont.)FIG. 631.—System  $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ ; revision of  $\text{CaO}\cdot 6\text{Al}_2\text{O}_3$  field.

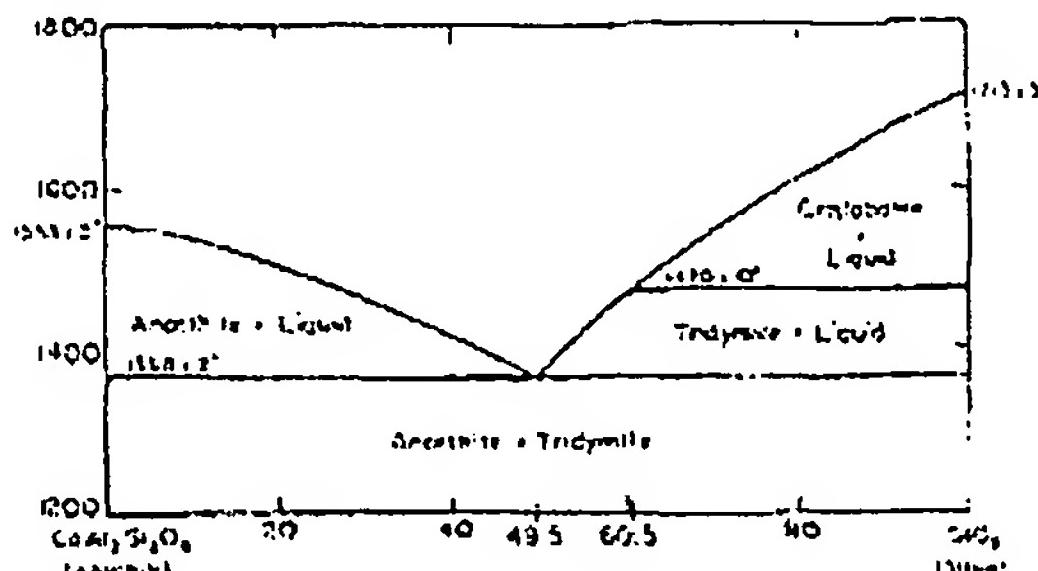
A. L. Gentile and W. R. Fuller, private communication, Dec. 12, 1981.

FIG. 632.—System  $\text{CaO}\cdot 6\text{Al}_2\text{O}_3$  (calcium hexaluminite)— $\text{CaAl}_2\text{Si}_2\text{O}_8$  (anorthite)— $\text{CaAl}_1\text{SiO}_4$  (gehlenite); revised.

A. L. Gentile and W. R. Fuller, private communication, Dec. 12, 1981.

FIG. 633.—System  $\alpha\text{-Al}_2\text{O}_3-\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ .

G. A. Reakin and P. E. Wright, Am. J. Sci., 6th Ser., 39, 47 (1915).

FIG. 634.—System  $\text{CaAl}_1\text{SiO}_4$  (anorthite)— $\text{SiO}_2$  (silica).

J. F. Schairer and N. L. Bowen, Bull. Soc. Geol. de Fin. Lande, 20, 71 (1947).

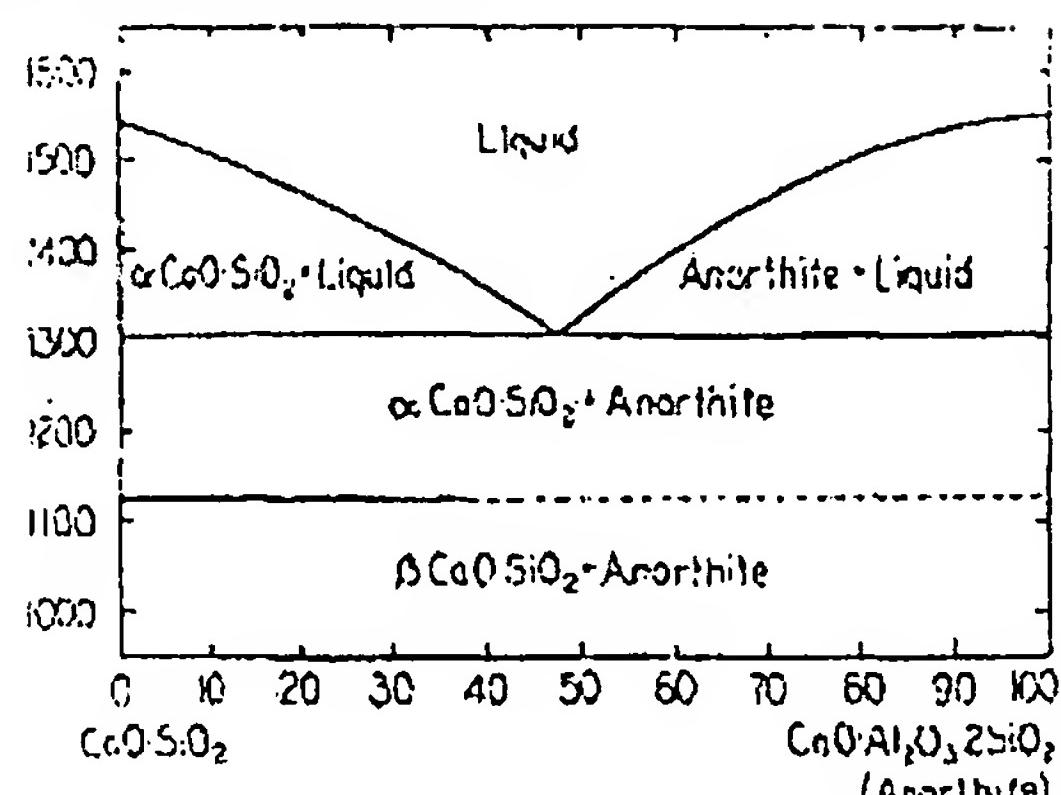
$\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  (concl.)

FIG. 635.—System  $\text{CaO}\cdot\text{SiO}_2\text{-CaO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ .  
E. F. Osborn, *Am. J. Sci.*, 240, 755 (1942).

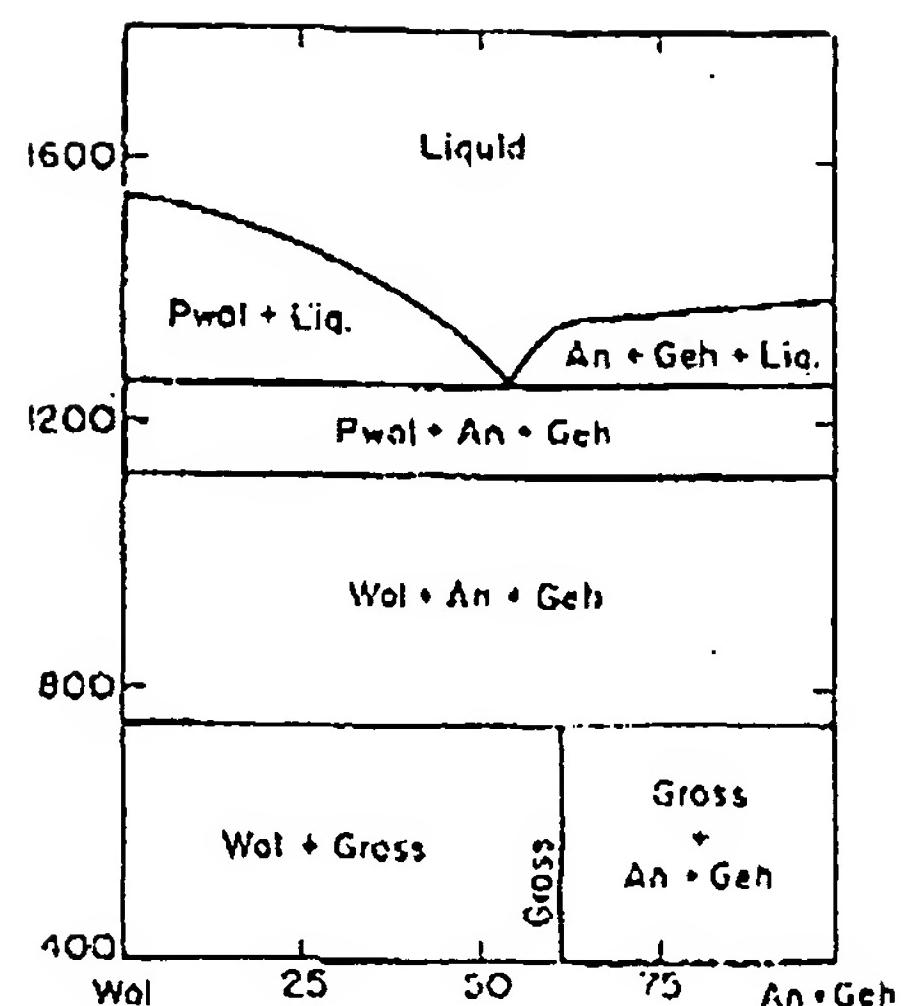


FIG. 638.—Pseudo-binary, (wollastonite)-(anorthite and gehlenite eutectic); postulated. Wol—wollastonite,  $\text{CaSiO}_3$ ; Pwo—pseudowollastonite,  $\text{Ca}_2\text{SiO}_5$ ; An—anorthite,  $\text{CaAl}_2\text{Si}_2\text{O}_8$ ; Geh—gehlenite,  $\text{Ca}_2\text{Al}_2\text{SiO}_7$ ; Gross—grossularite,  $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$ .

H. S. Taylor, Jr., *J. Geol.*, 58 (3) 225 (1950).

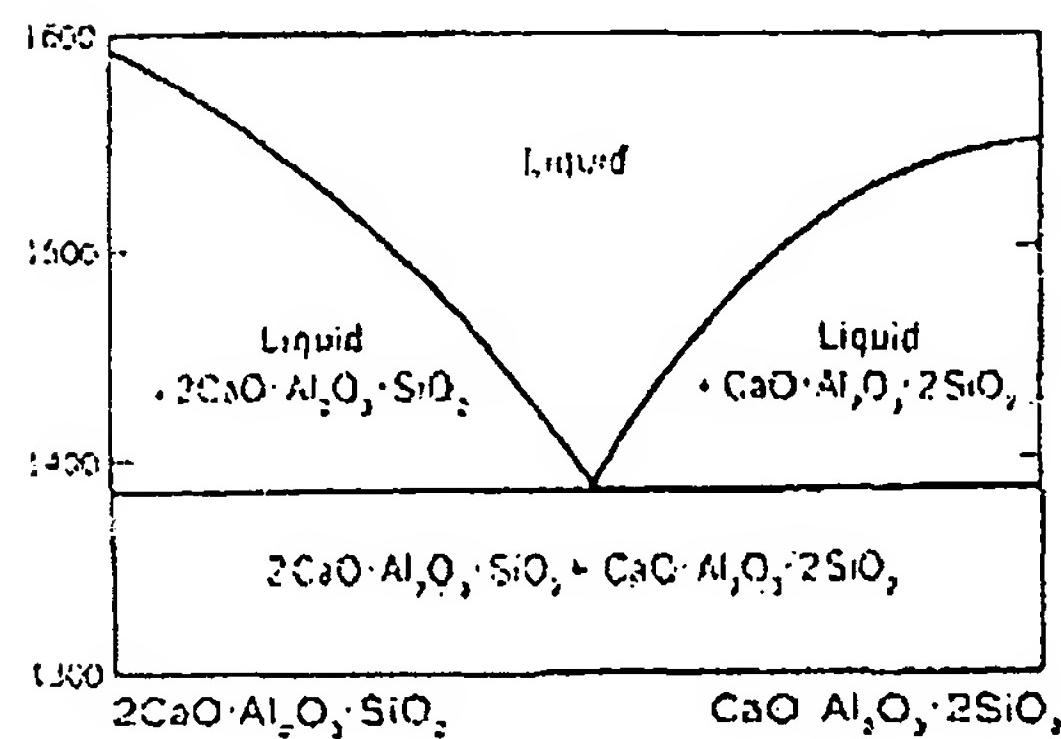


FIG. 636.—System  $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2\text{-CaO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ .  
G. A. Rankin and F. E. Wright, *Am. J. Sci.*, 4th Ser., 39, 49 (1915).

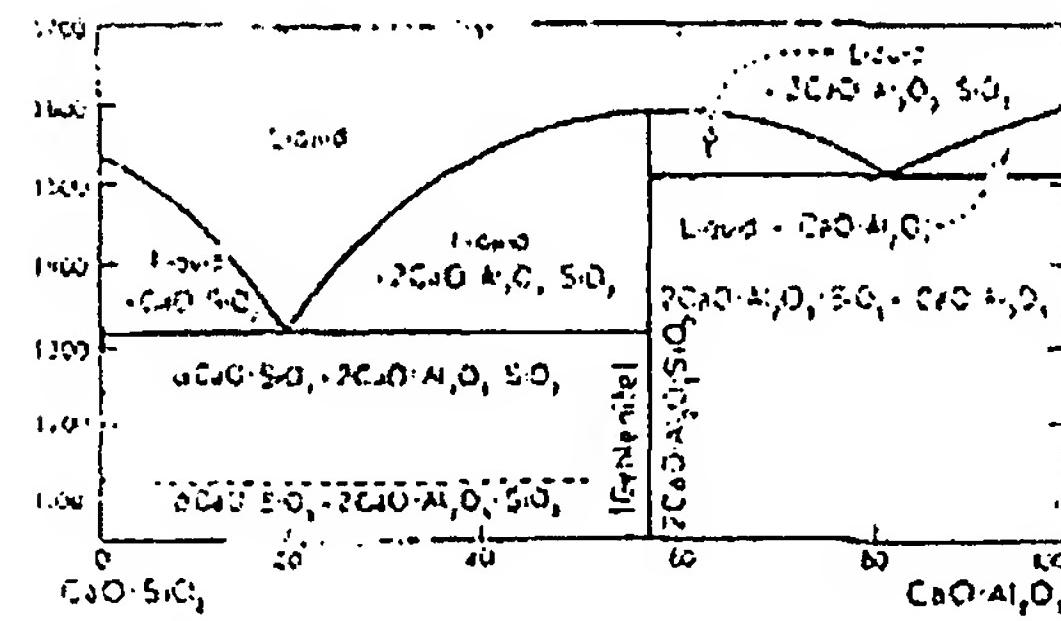


FIG. 637.—System  $\text{CaO}\cdot\text{SiO}_2\text{-CaO}\cdot\text{Al}_2\text{O}_3$ .  
G. A. Rankin and F. E. Wright, *Am. J. Sci.*, 4th Ser., 39, 50 (1915); modified by E. F. Osborn and J. F. Schairer, *ibid.*, 239, 721 (1941).

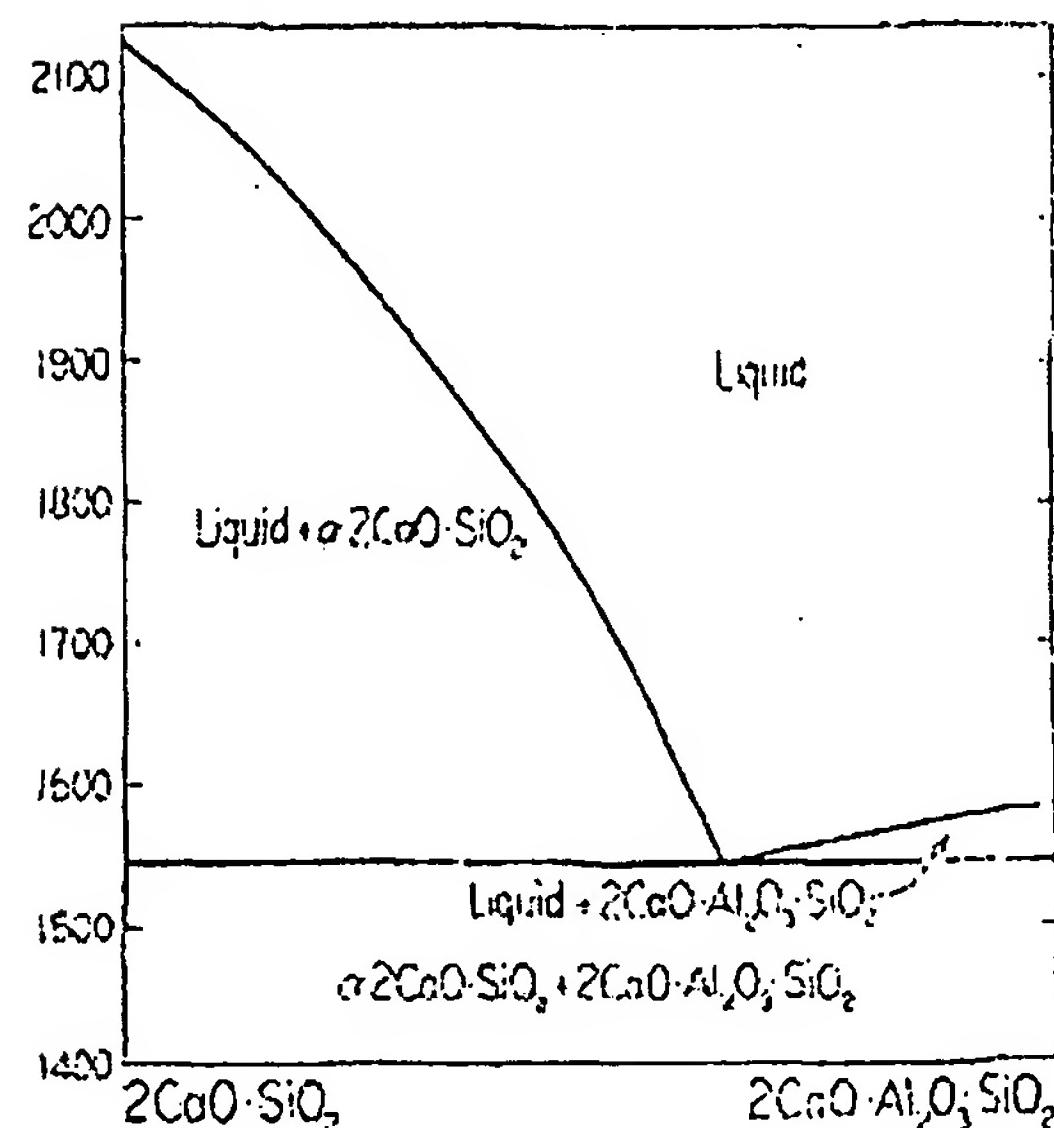


FIG. 639.—System  $2\text{CaO}\cdot\text{SiO}_2\text{-}2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ .  
G. A. Rankin and F. E. Wright, *Am. J. Sci.*, 4th Ser., 39, 47 (1915).